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Geochemistry of Carbonate Sediments and Sedimentary Carbonate Rocks

Part III

Minor Element Distribution

Donald L. Graf

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GEOCHEMISTRY OF CARBONATE SEDIMENTS AND SEDIMENTARY CARBONATE ROCKS

Part III – Minor Element Distribution



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FOREWORD

Detailed knowledge of the chemical and mineralogical variations that exist in the carbonate rocks limestone and dolomite and of the processes responsible for this diversity is fundamental to the Illinois State Geological Survey's program of furthering the practical utilization of these natural resources of the state. Chemical composition is particularly important when the rocks are used as agricultural limestone and fluxing stone or in the manufacture of dolomite refractories, lime, calcium carbide, sodium carbonate, glass, and other products.

The invitation extended to Dr. Graf by the United States Geological Survey to prepare the chapter on sedimentary carbonates for their revision of F. W. Clarke's "Data of Geochemistry" has afforded a valuable opportunity for the state and federal geological surveys to cooperate in a basic review of selected topics in carbonate geochemistry. The resultant material is presented in five Illinois State Geological Survey Circulars and subsequently will serve as the basis for a condensed treatment in the revised "Data of Geochemistry."

Part I, published as Circular 297, includes an introduction and sections on carbonate mineralogy and carbonate sediments.

Part II, Circular 298, includes the section on sedimentary carbonate rocks.

Part III deals with the distribution of minor elements.

Part IV will discuss isotopic composition, present chemical analyses, and also will contain the bibliography for the first four circulars.

Part V, concerned with aqueous carbonate systems, will be published with its own bibliography at a later date.



John C. Frye, Chief

GEOCHEMISTRY OF CARBONATE SEDIMENTS AND SEDIMENTARY CARBONATE ROCKS

Part III – Minor Element Distribution

Donald L. Graf

ABSTRACT

The distribution of major and minor elements in sedimentary carbonate rocks and the mechanisms responsible for this distribution are considered on the basis of published information contained in geologic studies, and in studies of present-day environments of carbonate deposition, isotopic composition of carbonates, and experimental aqueous and nonaqueous carbonate systems. There are five parts in this series of reports; an extensive bibliography for the first four parts appears in Part IV. Part V carries a separate bibliography.

INTRODUCTION

The concentrations of minor elements found in carbonate rocks are a function of the amounts in solid solution in the carbonate minerals and of the kinds and amounts present of detrital minerals, accessory authigenic precipitates, noncarbonate skeletal material, organic matter, phases formed during diagenesis, and elements adsorbed upon all these materials. A given minor element present in a carbonate rock is frequently distributed among materials formed at several different times by several different mechanisms. Evaluation of the minor-element content of each of the materials is difficult and the attempt has not often been made (see Correns, 1956; Le Riche, 1959). Hirst and Nicholls (1958) considered the material that was not soluble in acetic acid to be essentially equivalent to the detrital fraction (table 36), and showed that the percentages of Co and Cr carried in the detrital fraction are considerably greater than those of Ni and V.

The work of Le Riche illustrates the difficulty of using statistical analysis unless the mechanisms operative in trace-element distribution are understood. He found that the amounts of Mo, V, Cu, and Ni in shales and argillaceous limestones of the Lower Lias of southern England correlated directly with organic carbon content and with the amount of CaCO_3 (see table 37). A series of leaching experiments with water, organic liquids, and acids showed first that none of the above four elements was present in significant amount in CaCO_3 ; Le Riche believed that decaying organic matter may have been involved in CaCO_3 precipitation and that the direct relationship is actually between organic matter and CaCO_3 . Almost all of the V appears to be combined with silicate minerals such as the clays, and Le Riche suggests it originally may have been present in organic matter and subsequently transferred.

Pure sedimentary carbonates seldom show marked concentrations of minor elements other than Sr (Krauskopf, 1955). Nicholls (1958) found that Sr and Mn were the only two trace elements out of ten studied that were present in greater amounts in a calcite-cemented sandstone than in the uncemented equivalent. The "coastal disease" of livestock in Australia results from a dual deficiency of Cu and Co in vegetation grown on indurated, wind-built dunes of comminuted shells and coral

fragments (Thomas, 1940). Indeed, Thomas attributed the fact that these dunes are able to migrate so far inland before becoming fixed by vegetation to the paucity of available plant nutrients rather than to aridity.

The crystal structures of both the rhombohedral and orthorhombic carbonates allow substitution of divalent cations of only a limited size range. Some of the larger cations such as Ba, Sr, and Pb are accepted in aragonite but are released during the subsequent conversion of that mineral to calcite.

From Krauskopf's (1955) evaluation of rare metal concentrations in sediments and sedimentary rocks and from the work of Goldschmidt (1937), Goldschmidt et al. (1948), and Blumer and Erlenmeyer (1950), carbonate materials rich in organic matter should also be enriched in Ag, As, Mo, V, Ni, Pb, Cu, Ge, Br, and I, whereas carbonate rocks and sediments containing manganese oxides should be enriched in Co, Mo, and Ba. Data on hand appear to be insufficient for evaluation of the manner in which minor element concentrations in phosphatic limestones are localized, except that much of the F and Cl is structurally contained within phosphate minerals. Various cations might be expected to form insoluble carbonates in nature, but rarely do so. Of these Krauskopf suggested that Ba may be preferentially adsorbed on clay minerals, and that metals such as Pb, Zn, Ni, and Cu may react with H_2S from decaying organic matter to precipitate as sulfides even more insoluble than the corresponding carbonates.

The relative probabilities of 13 minor elements' being incorporated into rocks as sulfide precipitates, as organic compounds, and as adsorbed material on hydrated Fe_2O_3 , hydrated MnO_2 , apatite, montmorillonite, plankton, or peat moss were further evaluated by Krauskopf (1956) from calculations and relatively simple laboratory experiments. In good accord with natural distributions are the ready adsorption of Cu, Zn, and Pb by all of the solids tested except plankton, the excellent adsorption of Co and Ni onto hydrated Mn and Fe oxides, and the readiness with which Ag is held by organic matter. Krauskopf concluded by a process of elimination that biologic processes and organic compounds must play a role in the concentration of V, Ni, Co, and Mo.

Keith and Degens (1959) found higher amounts of Co, As, Ag, and Cu in pyrite from freshwater shales and limestones than in comparable marine rocks. They suggested that there may be differences in the initial trace-element assemblages collected in marine and nonmarine environments by organic matter and other chemical scavengers, and that these elements were released by decay and incorporated in the sulfides.

A study of the minor-element variation across a limestone-to-dolomite transition in a single bed was made by Adams and Lewis (cited in Adams et al., 1959), who found that the average U content was higher and the individual values more variable in the dolomite than in the limestone. Thorium was unique among some 20 elements studied in showing no change in average concentration or range of values across the transition.

Mohr (1956) noted that the relatively small amounts of Co, Ni, Cu, and V found in the $MnCO_3$ -rich beds of the Lower Cambrian in North Wales are more typical of carbonate sediments than of manganese oxidates. Sr and Ba showed extreme variation among the samples examined, whereas Cr varied but little. Zr is unusually high and is shown by analysis to be associated with the spessartine; there is no detrital zircon. The Mo value is high, compared with that for typical limestone, which agrees with the results obtained by Kuroda and Sandell (1954) for manganese-iron carbonate concretions.

MINOR-ELEMENT ADSORPTION ON CARBONATES

The retention of minor elements by cation adsorption on calcite and dolomite is obviously not very great, particularly in view of the extensive recrystallization to larger particle sizes that commonly occurs in these materials and that apparently results in extraneous cations' either being taken into solid solution or rejected altogether. Walton and Broecker (1959), for example, found a close correlation between clay content and the concentration of alpha-emitters in carbonate-rich Atlantic deep-sea core Al80-72. Few data are available that clearly measure adsorption on carbonates. Adsorption measurements must be carried out in solutions in which equilibrium has first been achieved between the solvent and the range of particle sizes and degrees of structural damage initially present in the solid, and the amount of added cation in solution must be less than that required to exceed the solubility product of any phase involving the added cation.

Correns (1924) was unable to measure an adsorption of Cu on calcite, and chemical reaction took place during the experiments of Heydemann (1959). Canals et al. (1949, 1950) used somewhat lower concentrations than Heydemann and believed that they were measuring true adsorption, but Heydemann is skeptical.

With the very low equilibrium Zn_{aq}^{++} concentration of 0.90×10^{-6} M at 25°C, Jurinak and Bauer (1956) measured an adsorption of about 500 ppm on calcite having a surface area of 6.78 m²/g. Progressively greater amounts of Zn^{++} were adsorbed on dolomite and magnesite, apparently because of the very close similarity in ionic charge and radius between Zn^{++} and Mg^{++} . The negative standard entropy values computed in the experimental calcite system suggested to these authors that the hydration shell around the Zn^{++} ion is still relatively intact after adsorption onto calcite, whereas the large positive entropy values in the dolomite system, and the still larger values in the calcian magnesite system, indicate progressively greater dehydration. The Zn adsorption of 500 ppm given by Jurinak and Bauer for calcite is some 20 times the average concentration of Zn in carbonate rocks. If this quantity is indeed a measure of adsorption, such Zn must be held loosely enough so that in natural environments it could readily be displaced during diagenesis or recrystallization.

BIOGENIC CONTRIBUTIONS

The potential importance of organisms in contributing minor elements to carbonate rocks and sediments is perhaps most strikingly shown by those carbonate materials made up almost entirely of the remains of a single organism. Twenhofel (1932, p. 305), for example, referred to Jurassic and Cretaceous beds consisting almost entirely of shells of *Gryphaea* or *Exogyra*. Monroe (1941) described a bed in the Eutaw Formation of late Cretaceous age in Russell County, Alabama, that is as much as 100 feet thick and is made up almost solidly of shells of *Ostrea cretacea*. Present-day wash on the shores of the Frisian Islands, consisting principally of the tests and spines of sea urchins (Hantzschel, 1936), may be compared with a rock composed chiefly of sea urchin spines near Villettes-les-Saint-Amour, France (Dreyfuss, 1933). Bucher (1938) referred to present-day and fossil concentrations of gastropods and of gastropod opercula.

The path followed after the death of an organism by the minor elements originally contained in the soft parts and in the skeletal material can be studied by analyzing present-day and fossil specimens of the organism.

Soft Parts of Organisms

Very little has been learned about what proportion of the various metals originally contained in the soft parts of organisms is finally retained within immediately adjacent lithified carbonate rocks. Considerable work has been done on minor-element distribution in the soft parts (Vinogradov, 1953; Nicholls et al., 1959) and their organic compounds have been described (Awapara and Allen, 1959; Lester and Bergmann, 1941; Kind and Bergmann, 1942; Bergmann and Feeney, 1949; Bergmann and Ottke, 1949; Bergmann et al., 1943; Bergmann and McTigue, 1948; Valentine and Bergmann, 1941; Bergmann and Stansbury, 1943; Bergmann and Burke, 1956; Bergmann et al., 1956; see Hanson, 1959, p. 108, on the general occurrence of hydrocarbons in living organisms). The persistence of organic materials for long periods in natural environments also is being studied (Vallentyne, 1957; Abelson, 1959a, 1959b; see discussion on amino acids in section on carbonate rocks).

Apparently the only organic materials thus far described that survive under favorable conditions for geologically long periods of time and carry specific minor elements are the porphyrins. Hematin and chlorophyll, the two most important porphyrin pigments, quickly lose their Fe and Mg to become metal free until V and Ni occupy the sites formerly populated by Fe and Mg (Abelson, 1959a, 1959b). The resulting stable complexes, hydrophobic and very soluble in petroleum in contrast to the relatively more hydrophilic metal-free porphyrins, generally are the preponderant types of porphyrin found in old sediments and petroleum (see Blumer, 1950, 1956; Dunning et al., 1954; Baker and Hodgson, 1959). Most of the porphyrins extracted from oil shale from Colorado, however, are complexed with Fe; the Ni-porphyrin complex identified in this shale by Moore and Dunning (1955) was present only in small amounts. The V and Ni contents of crude oils and asphalts generally are higher than those of the rocks in which these materials are found (Erickson et al., 1954; see table 24). Treibs (1935, 1936) identified porphyrins in sedimentary rocks as old as the Cambrian.

Skeletal Material

The concentrations of elements in the skeletal material of living organisms can be compared relatively easily with that in fossil material, and available information on this subject, particularly for Sr, has been incorporated in the detailed summaries that follow. A discussion of the concentration of Mg in skeletal materials will be found in the section on carbonate rocks. Vinogradov (1953) and Clarke and Wheeler (1922) give numerous additional references on skeletal composition. It should be remembered that skeletal material may contain a sizeable percentage of structural protein or its degradation products, and that part or all of some of the minor elements listed may be bound up with the organic matter. Goldberg (see Krumholz et al., 1957; Goldberg, 1957) estimated from recent literature that the concentration factors relative to sea water for the skeletal material of marine invertebrates are Sr and Zn, 1,000; Cu, 5,000; Ni, 200 (Laevastu and Thompson, 1956); S, 1; I, 50. For the skeletal material of marine vertebrates, concentration factors are Sr, 200; Zn, 30,000; Cu, 1,000. Bevelander and Benzer (1948) showed that changing the constituents of sea water produces a change in the composition of shells formed by mollusks.

A method of determining whether the original compositions of certain marine fossils have changed was described by Lowenstam (1959). The O^{18}/O^{16} ratios and the amounts of Sr and Mg in solid solution in present-day articulate brachiopods are all temperature-dependent. Diagenetic alteration by fresh water would result

in O^{18}/O^{16} values corresponding to spuriously high temperatures and in Sr and Mg contents giving spuriously low temperatures. If, therefore, the temperature of formation indicated for a fossil by the O^{18}/O^{16} ratio agrees with that determined from either Sr or Mg concentration (or with both of these determinations), then the oxygen isotopic composition and the minor elements concentration(s) yielding concordant temperature values have not changed during burial. Furthermore, the isotopic and minor element composition of an ancient ocean in which material giving concordant temperature values was deposited must have been much like that today. Good temperature agreement is obtained by Lowenstam from all three measurements on a *Chonetes* of late Mississippian age. Temperatures derived from O^{18}/O^{16} and Sr measurements agree reasonably well for four other Cretaceous and Permian fossils.

MINOR-ELEMENT CONCENTRATIONS IN ORGANIC MATERIAL

A good example of minor-element concentration in organic material is given by the carbonaceous nodules found sparsely disseminated in early Permian argillaceous limestones, shales, and sandstones of southwestern Oklahoma, which contain from 0.37 to 0.86 percent U (Hill, 1957; C. A. Horr, U. S. Geological Survey, analyst). The ash from various nodules has concentrations of U, V, As, Co, Ni, Pb, Fe, and Y in the 1 to 10 percent range (A. T. Myers, P. J. Dunton, P. R. Barnett, U. S. Geological Survey, analysts). Most of the asphaltite is associated with secondary celestite and anhydrite that fill fractures and solution cavities in dolomites and cement the siltstones. Uraninite and smaltite have been identified from X-ray diffraction patterns of the nodules, which are believed to be epigenetic because of their botryoidal surfaces, concretionary structure, and concentration along fractures and permeable zones. The underlying Paleozoic rocks are highly petroliferous. One nodule with an ash content of 44.08 percent was found to contain 41.61 percent C and 2.90 percent H, a ratio of 14.4 (E. A. Brittin, U. S. Geological Survey, analyst).

Four samples of the Green River Formation from John Hay, Jr., well No. 1, Sweetwater County, Wyoming, which contain from one to seven percent organic matter and little more than 50 percent calcite and dolomite, were analyzed spectrographically by Janet D. Fletcher (U. S. Geological Survey, unpublished data; see analysis 73, Part IV). Ranges and average values for some minor elements, in ppm, are markedly higher than those that will be described later for relatively pure carbonate rocks. For Cu, the range is 130 to 380, the average, 250; for B, range 20 to 100, average, 70; for V, range 60 to 90, average 70; for Cr, range 30 to 50, average 40; for Ni, range 20 to 50, average 40.

DETRITAL MINERALS

That portion of the trace-element content of carbonate rocks derived from detrital minerals is a complex function of the nature of the sediment source area and the nature and duration of transport. In many carbonate rocks the detrital minerals are the principal sources of minor elements, and yet it is difficult to discuss these minerals in detail. An exhaustive discussion would incorporate compositional data for all sedimentary materials even moderately resistant to transport, an obviously impractical procedure.

AUTHIGENIC MINERALS AND ACCESSORY CHEMICAL PRECIPITATES

The possible chemical precipitates and authigenic minerals in carbonate rocks and sediments are more amenable to discussion. The occurrence of fluorite

and celestite in dolomites from evaporite sequences, discussed in detail below in the sections on F and Sr, is a reasonably well documented example of original chemical precipitation of accessory minerals in carbonate sediments. Arrhenius et al. (1957) listed zeolites, manganite, goethite, barite, anatase, rutile, and possibly some clay minerals, as solids that are precipitated from solution in sea water, at the sediment surface, or in the sediment.

Boswell (1933) described sharp-edged euhedral crystals of tourmaline from limestones. On the basis of petrographic evidence, analcite, chabazite, phillipsite, other zeolites, phosphates, pyrolusite, gypsum, hematite, limonite, feldspars, micas, quartz, sphene, anatase, rutile, brookite, the glauconite-greenalite-chamosite-chlorite group of minerals, clay minerals, carbonates other than dolomite and calcite, tourmaline, and the pyrite-pyrrhotite-marcasite group have been called authigenic minerals in sedimentary rocks (Boswell, 1933). Some authors have listed epidote, garnet, staurolite, and hornblende as well.

Vasil'ev et al. (1956) reported from their studies and those of earlier workers that small amounts of zeolites are widespread in Mesozoic and Cenozoic rocks of variable lithology in the northern Caucasus, western Kazakhstan, the Volga region, and the Penza area. Analcite crystals are found, together with crystals of calcite and dolomite, encrusting pores in the limestone of Great Bogdo Mountain (Kolbin and Pimburskaya, 1955) in an area unaffected by vulcanism or metamorphism.

Sepiolites typically are found as diagenetic products in Mg-rich sediments, such as those of Lake Kulundinsk (Rateev, 1954), and in dolomites and dolomitized limestones (Rateev and Kotel'nikov, 1956). Occurrences of sepiolite in the dolomites of the lacustrine Green River Formation in Wyoming (Bradley, 1929b; Milton, 1957) and in the lacustrine dolomite of the Silkstone Series of Tertiary age from near Ipswich, Queensland (Rogers et al., 1954) support this generalization. Rateev found palygorskites, on the other hand, to be more abundant in marine marls having a typical maritime fauna.

The minor-element composition of limestones will be altered by post-depositional formation of major mineral constituents such as collophane and dolomite. Ames (1960) used radioisotopes to study the uptake of Pm^{+3} , Sr^{+2} , U^{+6} , and Pu^{+4} during the formation of phosphorite from calcite.

Sedimentary Sulfides

There are widespread occurrences in carbonate rocks of small amounts of metallic sulfides and H_2S , the latter in fetid limestones. Krauskopf (1955) suggested that the small grains of galena, sphalerite, millerite, and linnaeite in such rocks may be formed when substituted Pb, Zn, Ni, and Co in aragonite are set free during conversion to calcite and are combined with traces of sulfur from organic matter in the sediment. Lamar and Shrode (1953) measured the amount of H_2S evolved when several fetid Paleozoic limestones were dissolved in acid. Expressed as weight percent of the original rock, the values obtained were 0.002 percent for the Kinkaid and Glen Dean Limestones, 0.003 percent for the Salem Limestone, and 0.012 percent for the Ste. Genevieve Oolite. The Racine Dolomite evolved less than 0.001 percent H_2S . None of the dolomites examined had a fetid odor.

The possibility remains that in such sulfide occurrences low-temperature hydrothermal activity may have taken place. However, the sulfides frequently occur in areas remote from intrusives or known ore deposits, and often are localized near siderite or organic matter. Goldschmidt (1937) reported that millerite, linnaeite, and arsenopyrite are often found in British coal. Other occurrences of millerite in unaltered sedimentary rocks are noted by Schraut (1950), Anderson

and Smythe (1942), Bagrowski (1940), and Northrup (1937). Sphalerite widely distributed in small amounts through limestones and other rocks of Devonian age in southeastern Tartariya is localized along cracks and other open spaces at places where there are siderite concretions, fossil remains, or bitumen, all indicating reducing conditions (Miropol'skiy and Miropol'skaya, 1951). It is commonly accompanied by pyrite and less often by chalcopyrite. Galena, sphalerite, pyrite, and barite are found in clay ironstone concretions in black, bituminous, thinly laminated shale of Pottsville age in Ohio (Ver Steeg, 1942). Galena, sphalerite, and chalcopyrite occur in the fossiliferous limestone of late Pennsylvanian age that forms the roof of a coal bed in a mine near Loving, Young County, Texas (Baker, 1933). Pyrite, sphalerite, and galena also are found in thin beds and nodular zones rich in siderite in the Middle Coal Measures of Nottinghamshire and Derbyshire (Edwards and Stubblefield, 1948).

Milner (1929) described authigenic pyrrhotite from sediments, Rubey (1930) found it in a pyritic and gypsiferous limestone, the Greenhorn Formation of late Cretaceous age in the Black Hills area, and Erd et al. (1957) described smythite and pyrrhotite from geodes in the Harrodsburg Limestone at a number of localities near Bloomington, Indiana, far removed from igneous rocks or evident hydrothermal activity. Also found in the Indiana geodes are sphalerite, anhydrite, siderite, dolomite, millerite, barite, marcasite, and pyrite.

Disseminated crystals of galena and sphalerite are found at correlatable horizons in the Lockport and Guelph Dolomites of Silurian age from eastern New York to western Ontario (Cannon, 1955), and additional occurrences are known in Iowa, Wisconsin, Illinois, and Ohio. In New York, the sulfides are concentrated, together with above normal amounts of Cr, Ni, Cu, Y, Fe, and other elements (table 1) in clastic zones of partially dissolved fossil debris and fine-grained carbonate that appear to have been deposited below wave base. Immediately overlying beds of recrystallized core and reef-flank material contain calcium sulfate and strontium and barium compounds, in addition to the sulfides. No specific relation of the metals to faults is apparent. The frequent association of sulfides with algal bioherms, less commonly with *Stromatopora* and corals, suggested to Cannon a syngenetic origin, possibly involving metal concentration by living algae and further precipitation and adsorption around decaying organic matter soon after burial in the sediments. Algal concretions being precipitated in Little Conestoga Creek, Lancaster County, Pennsylvania, were found to contain 46 ppm Zn and 7.5 ppm Pb, although the stream contained only 0.06 ppm Zn. Marl in Bergen Bog, Orleans County, New York, overlying glacial clay that in turn overlies the Lockport Dolomite, had 180 ppm Zn and 2 ppm Pb, both expressed in terms of dry weight.

Caprock Mineral Assemblages

The typically nonfossiliferous limestone that forms one zone of the caprock of many salt domes is noteworthy because the suite of accessory minerals it contains, which must be of sedimentary origin, albeit a complex one, is similar to that found in geodes and disseminated throughout limestones. The limestone portions of the caprocks of Texas and Louisiana salt domes commonly contain crystals of sulfur, barite, celestite, anhydrite, strontianite, aragonite, galena, sphalerite, and less commonly a number of other sulfides (see Hanna and Wolf, 1934, 1938; Taylor, 1938). Calcite and sulfur may replace anhydrite, and anhydrite protected by sulfur is often the only evidence of anhydrite left in a mass of calcite (Brown, 1931). The limestone at Heckley Dome, Harris County, Texas, contains oil-filled vugs in addition to minor amounts of barite and strontianite (Stenzel, 1943). Rols-

hausen (1934) described a zone of siderite with minor impurities in the caprock at Carlos Dome, Grimes County, Texas (see analysis 91, Part IV).

Sedimentary Sulfur

The occurrence of native sulfur in sedimentary carbonate rocks other than caprocks probably is much more widespread than is generally realized. Steinbrecher (1959) described S crystals associated with calcite in a fetid limestone encountered in a drill hole on the South Harz border, Germany. Celestite and S crystals are found in gypsum rocks of Miocene age in Poland that are partially replaced by carbonate (Laszkiewicz, 1957). At the Woolmuth quarry, Monroe County, Michigan, celestite leached from SrSO_4 -rich beds higher in the section has been deposited with calcite and S in cavities in bituminous siliceous dolomite (Kraus, 1905b). Sulfur at Ras Gamsa, Egypt, is found disseminated in anhydrite and in open spaces in beds of aragonite and dolomite. Some portions of these sulfur-bearing rocks at Ras Gamsa are extensively contaminated by hydrocarbons (Schnellman, 1959). Aprodov (1947) described small gypsum pseudomorphs after gypsum in Permian age marls of the upper Chusovoya River region of the U. S. S. R., and Bonython and King (1956) reported the occurrence of gypsum-encrusted sulfur nodules in clays of Recent age on the shore of Lake Eyre, South Australia.

The descriptions of most of these occurrences indicate that the sedimentary S is associated with bituminous matter, with either calcium or strontium sulfate, and with calcium carbonate. Acceptance of a mechanism involving bacterial sulfate reduction, accompanied by oxidation of organic matter, release of CO_2 , and subsequent carbonate formation involving the CO_2 , has long been advocated by some geologists. The isotopic compositions of carbonate carbon from caprock, which is remarkably light, and of the accompanying S can be explained satisfactorily by this mechanism (see section on isotopic composition, Part IV). The S from the Australian locality described above by Bonython and King has a $\text{S}^{32}/\text{S}^{34}$ ratio of 22.98, indicating an organic origin for the S. Silverman et al. (1960) found isotopically light carbon in the carbonate cementing several sandstones and in a thin dolomite bed at the base of the Cloud Chief Gypsum on the Cement Anticline, Caddo County, Oklahoma. They believed that the CO_2 of the carbonate was derived in part from organic matter, but by chemical rather than bacterial oxidation.

In summary, then, isotopic carbon values indicate the generation of CO_2 from organic matter in sedimentary carbonate rocks at several localities; where native sulfur with an isotopic composition indicating organic origin is also present, a mechanism involving bacterial reduction of sulfate is favored.

The Green River Formation

Striking evidence for authigenic formation of a wide variety of compounds in carbonate sediments has been furnished by the studies of Charles Milton, J. J. Fahey, and their co-workers at the U. S. Geological Survey on the Green River Formation of Utah, Wyoming, and Colorado (Milton, 1957; Milton and Eugster, 1959; Milton and Fahey, 1960). The list of minerals deemed authigenic, typically because their sharply defined crystal boundaries cut sedimentary textures or because such crystals feather out into the groundmass, is given in table 2. The list includes a number of new minerals, and a number previously recorded only from rocks formed at much higher temperatures. Many of the beds of the Green River Formation contain more than 50 percent calcite and dolomite, but it cannot be assumed that all minerals listed in table 2 have been found as accessories in such beds.

The Green River Formation is a cold-water deposit formed in a lake that received periodic falls of volcanic ash and that for part of its existence had no outlet. There are no dikes or other evidence of volcanic activity, and the nature of the large amounts of hydrocarbons preserved in these beds indicates that no metamorphism took place (Hunt et al., 1954).

Milton and Eugster (1959) discussed the probable phase relations among the precipitates and diagenetic products formed by interaction of sodic solutions, common carbonate muds, and silica contained in volcanic ash, detrital minerals, and river water. Mineral associations and modes of occurrence are dissimilar in the several separate basins; the differences between those in Utah and Wyoming, for example, can best be explained as a consequence of greater depth in the Utah lake. The occurrence of nahcolite as small isolated masses in dolomite, rather than as persistent beds, may have resulted from the dehydration of brine isolated into pockets by continuous precipitation of dolomite mud. The boron of the Green River waters reacted with silica to form borosilicates; no borates are observed. The almost constant association of chalcedony and analcite, and the virtual absence of albite, are noteworthy.

DEEP-SEA SEDIMENTS

The distribution of minor elements in deep-sea calcareous sediments has been clarified by Arrhenius et al. (1957) who showed that the microcrystalline fluorapatite of a sample of bathypelagic fish debris had adsorbed ionium and other Th isotopes, together with 0.6 to 1.5 percent Zn, 0.1 to 0.5 percent Cu, several percent of rare earth elements, 0.05 to 0.15 percent Sn, and 0.03 to 0.10 percent Pb by the time it was incorporated in the top stratum of sediment. The rare earths, some U, and most of the Sr and Ba in the fish debris were associated with the fluorapatite, whereas the hydrocarbon filling of the bone cavities contained the Zn, Sn, Pb, Ti, Cu, Ag, some of the U, and much of the Mg, Al, Cr, and Ni. With long exposures at great ocean depths on surfaces of especially low rates of accumulation, such apatite apparently dissolves and the heavy metals are resorbed in the secondary layers of manganites.

In the pelagic oozes, which accumulate somewhat more rapidly, the fish debris with its adsorbed metals is largely preserved and the manganese oxide micronodules contain smaller amounts of rare earth elements.

Pratje (1939) said that red clay can be regarded as the insoluble inorganic residue remaining after the calcareous parts of foraminifera, coccoliths, and pteropods in *Globigerina* ooze have been dissolved away. If this statement is accepted, the considerable body of analytical data for red clays may be applied to calcareous oozes for which the percentage of acid-insoluble residue is known. However, Pettersson and Rotschi (1952) found that the Mn content of *Albatross* cores, calculated on a noncalcareous basis, was one-third to one-fifth as much as that in red clays. In any event, the analyses used in such calculation should be of red clay sampled as close as possible to the calcareous oozes being considered, for Wedepohl (1958) showed that there are constant differences between the trace element contents of Atlantic and Pacific marine clays. Differences in sedimentation rates and in the kinds and amounts of volcanic activity are suggested as explanations. The high minor-element contents of *Globigerina* and *Globigerina* oozes found by Wedepohl (1955) (table 29) are puzzling, for some of the individual values are higher than the comparable averages for red clay.

Deep-sea sediments contain black, Ni-rich magnetic spherules that have an average diameter of about 45 microns and are believed by many authors (for example, Fredriksson, 1959; Laevastu and Mellis, 1959) to be extraterrestrial. However, the similarity among Ni/Cu, Ni/Co, and Cu/Co ratios for *Globiğerina* ooze, red clay, and average igneous rock, contrasted with the values for average meteorite, indicate a terrestrial origin for the Ni, Co, and Cu in deep-sea sediments (Smales et al., 1957) (table 3). The Ni contribution from the spherules appears to be insignificant relative to that scavenged by manganese and iron oxides.

DISTRIBUTION OF SPECIFIC MINOR ELEMENTS

Discussions of the distribution of a number of specific elements are given below. In some instances where several elements were determined on the same set of samples, the results are presented as a separate table. Most of these tabulated results (tables 12, 16, 19, 22-37) are not discussed in the sections on specific elements, but they were considered in making the estimates of average abundance that are given later. The numerous determinations of Ni, Co, V, Cr, and Mo in carbonate rocks given by Goldschmidt et al. (1948) are unfortunately only semiquantitative and have not been summarized here.

Alkali Metals

A composite of 32 German limestones of Devonian age contained 43 g/ton Li_2O (10 ppm Li), a composite of 16 German limestones of Cretaceous age, 76 g/ton (17.5 ppm Li), a composite of 45 German Jurassic age limestones, 50 g/ton (11.5 ppm Li), and a chalk from Kvarnby, near Malmö, Sweden, 3 g/ton Li_2O (0.7 ppm Li) (Strock, 1936). Two limestones examined by Higazy (1954) each contained 1 ppm Li. Landergren (1948) reported 100 ppm Li and 5 ppm Rb in marine siderite ores.

Horstman (1957), using a flame photometer, was unable to detect Li, Rb (<5 ppm), or Cs (<1 ppm) in seven of Goldich and Parmelee's (1947) limestones and dolomites, which contained from 1 to 5 percent insoluble residue consisting almost entirely of silica minerals. These elements would in less pure carbonate rocks be associated principally with clays and related layer lattice minerals. Thus, a limestone of Lower Ordovician age from Stenbrottet, Sweden, locally contains 50 percent or more of glauconite, which in two samples was found by Herzog et al. (1958) to have 307 and 311 ppm Rb. Of this Rb, 87.8 and 86.9 ppm were Rb^{87} .

Welby (1952, 1958) found in a composite sample of Austin Chalk from various localities, in wt percent, Na_2O , 6.36; K_2O , 2.45; Rb_2O , 0.022; Li_2O , 0.0065; and Cs_2O , trace. For a similar composite sample of Selma Chalk, the values were Na_2O , 1.50; K_2O , 1.75; Rb_2O , 0.020; Li_2O , 0.014; Cs_2O , 0.00089. The averages and ranges for 19 samples of *Globiğerina* ooze are Na_2O , 3.57 (2 to 5.5); K_2O , 2.11 (0.25 to 4.50); Rb_2O , 0.026 (0.005 to 0.050); Li_2O , 0.013 (0.004 to 0.028). Cs_2O was below the limit of detection in seven samples, and reached a maximum of 0.0018 percent. When the possible Cs_2O concentrations in the seven samples are taken into account, the average value obtained is 0.00066 ± 0.00004 percent. Welby did not remove salt water from his core samples. He calculated that if the water were 100 percent of dry weight, only the 1.07 percent Na_2O left on evaporation would be significant in terms of the *Globiğerina* ooze determinations cited above. Welby also observed from scatter diagrams that lithium is not geochemically coherent with the rest of the alkalis in these samples. He concluded that the alkali metals are associated principally with the clay frac-

tion of the sediments, although also present in detrital feldspar and possibly concentrated in the skeletal material of some organisms.

McKerrow et al. (1956) found that trilobites from the Upper Silurian age Wenlock Limestone at Dudley, Staffordshire, England, are markedly enriched in Cs relative to other alkali metals. The average of Rb/Cs ratios for the trilobites is 3.9, the geometric mean, 2.4. For samples of the enclosing sediment, the comparable values are 19 and 15. Canney (1952) obtained a closely similar average Rb/Cs ratio of 15 for 323 sedimentary rocks. The K/Rb ratio of the trilobites studied by McKerrow and his co-workers is not significantly different from that of the enclosing sediment, and is about the same as that in igneous rocks and other sediments. Accumulation of Cs by the trilobites is believed to have occurred during growth, rather than by selective adsorption after death, which would have been expected to impoverish the matrix. Of five brachiopods also examined, only *Lingula*, the only chitinous form among the five, showed some Cs enrichment. The averages and ranges of the actual spectrographic analyses are, for the trilobites, Li, 11 (3 to 25); Na, 2000 (1400 to 2700); Rb, 34 (8.5 to 100); and Cs, 25 (4 to 80) ppm. For the matrices they are Li, 22 (1 to 30); Na, 3100 (2500 to 3600); Rb, 45 (<1 to 62); and Cs, 6 (<1 to 14) ppm.

Limestones of Paleozoic age from Illinois examined by Lamar and Shrode (1953) contained an average of 80 ppm (range 40 to 150 ppm) water-leachable Na^+ , and 30 ppm (10 to 80 ppm) water-leachable K^+ . The comparable averages and ranges for Paleozoic age dolomites from Illinois are 130 ppm (70 to 240 ppm) Na^+ and 40 ppm (20 to 60 ppm) K^+ .

See also tables 1, 5, 19, 23, and 34.

Antimony

A composite of six samples of *Globigerina* ooze from the Pacific Ocean contained 1.1 and 0.2 ppm Sb in duplicate photometric determinations made using rhodamine B (Onishi and Sandell, 1955b). The comparable values for a composite of nine limestones and dolomitic limestones are 0.2 and 0.3 ppm, with 2.3 ppm As and a Sb/As ratio of about 0.1. Shales and deep-sea red clays both contain 5 to 10 times as much Sb as the carbonates mentioned, so that highly argillaceous carbonate rocks and sediments should have proportionately enhanced Sb contents.

See also table 22.

Arsenic

Only 1 or 2 ppm arsenic are found in carbonate rocks, unless carbonaceous material, iron oxides, or sulfides are present (Onishi and Sandell, 1955a). Dover Chalk (0.3 ppm) and Bedford oolitic limestone (0.6 ppm) fall at the lower end of the range observed by these workers. The single anomalously high value of 14.5 ppm for a gray limestone from Onondaga County, New York, is unexplained.

Heide and Moenke (1955) found from 0.21 to 1.99 ppm As in five pure or nearly pure Muschelkalk limestones from Steudnitz, near Jena, with an average of 1.0 ppm. A high As content was related to high values of Fe in analyses, except for one sample in which the Fe was present in ankerite (see also Goldschmidt, 1937, on the concentration of As in sedimentary iron ores). Wyllie (1941) measured from 0.3 to 7.0 ppm As in 17 North American limestones. Headen (1910), cited in Tremerne and Jakob (1941), found from 2.5 to 10.0 ppm As (average 5.1 ppm) in four marls from Kansas and Colorado.

Five shallow-water sediments containing more than 60 percent CaCO_3 showed an average of 4.1 ppm As, and five deep-sea sediments of similar composition averaged 4.2 ppm (Correns, 1937).

Barium

The most common Ba-carrying mineral in sedimentary rocks is barite, BaSO_4 , which may carry considerable amounts of Sr in solid solution (Dragunov and Katchenkov, 1953). Barite is commonly seen as vein fillings and replacements in limestones, and also has been observed as a coating in caves (Buckley, 1909; Evans, 1946b). Very thin films of fine-grained barite cut pre-existing textures in the late Tertiary capping-caliche of the Great Plains (Swineford et al., 1958). In a sample of this pisolitic rock from Hamilton County, Kansas, 2 percent of the rock was BaSO_4 . In all of these occurrences, barite obviously has undergone redistribution from unknown earlier Ba sources. Ba commonly shows an unusually wide range of concentrations compared with ranges for other elements; Young (1954) found from 0.1 to more than 2.0 percent Ba in red clays.

A parallelism between the percentage of Ba and the percentage of insoluble residue exists for the carbonate rocks of the Russian Platform (Vinogradov et al., 1952) (fig. 1). The amounts of Ba present are sufficient to give a concentration in the insoluble residue closely similar to that typically found in clays. Ba is one of the elements in these rocks the concentration of which is believed to be dependent upon the tectonic history of the platform. The high Ba value found by von Engelhardt in the clayey interlayer of the *Ceratites* limestone (see table 4) also is significant in this respect.

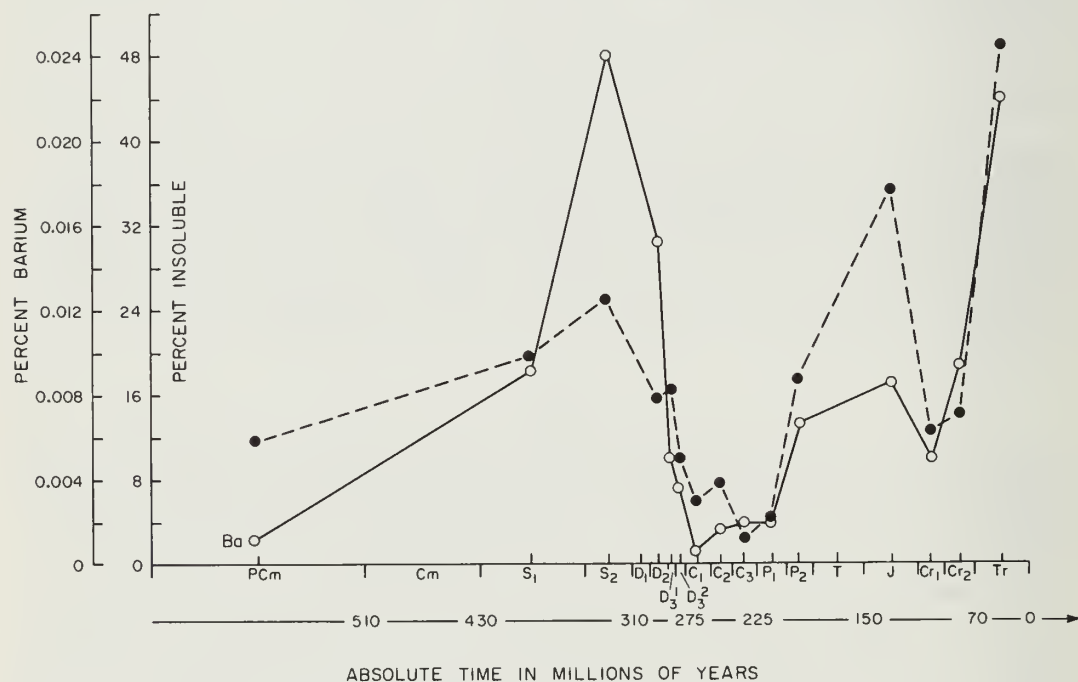


Fig. 1 - Variation with time of the Ba and insoluble residue contents of carbonate rocks of the Russian Platform (Vinogradov et al., 1952), based on 90 composite analyses of 3530 samples.

The correlation between CaCO_3 and high Ba concentrations in east equatorial Pacific sediments led Revelle (1944) to suggest that Ba in these sediments had been precipitated as carbonate. In 1955 Revelle and his co-workers noted strikingly high Ba values in siliceous sediments fringing calcareous ooze areas in the Pacific, 1 to 2 percent Ba in contrast to the usual 0.05 to 0.30 percent in pelagic sediments. They suggested that, because of the relatively low solubility of BaSO_4 , minute amounts of Ba in the calcareous skeletons of marine plankton might become concentrated when CaCO_3 was dissolved, so that high Ba would be expected where rates of both deposition and dissolution of CaCO_3 were high.

If the percentage of TiO_2 is used as a correction for varying accumulation rates, and the BaO/TiO_2 ratios of the surface layer of sediment across the belt of high organic productivity in the euphotic zone of the equatorial divergence (Arrhenius, 1952; Nielsen, 1952) are considered, the rate of Ba accumulation at the equator is found to be 20 times that outside the belt 10° N to 10° S and the increase toward this maximum is quite regular. The calcite of foraminifera and coccolithophoridae is practically free from Ba (see Wedepohl, 1955), and it is not known which organisms originally concentrate the Ba. A Miocene pelagic coccolith ooze, 99.5 percent soluble in weak acetic acid, contained 0.020 percent BaO, practically all of which was in transparent, greenish yellow, 5 to 15μ diameter aggregates of relatively low bulk density containing minute, highly refractive inclusions. If these aggregates are barite-containing fecal pellets, at least a mechanical concentration of Ba by benthonic organisms occurred.

If CaCO_3 is plotted against BaO/TiO_2 for a number of cores containing alternating clayey and calcareous strata, the most recent CaCO_3 productivity maximum has a corresponding BaO/TiO_2 maximum, the next older has a barely noticeable BaO/TiO_2 maximum, the third one, no BaO/TiO_2 maximum at all. The relatively high post-depositional Ba mobility shown by this leveling of original concentration gradients in about 200,000 years also is evidenced by the high content of α -active nuclides, presumably Ra and its successors, in the microcrystals of the Ba-bearing pellets (Arrhenius et al., 1957). The nuclides occur too deep in the core to have been taken up from sea water and must have been released by adjacent ionium-bearing minerals (Arrhenius and Goldberg, 1955). The frequent α -activity highs found in structures believed to have been formed by burrowing organisms are further evidence of the concentration of both Ra and Ba in excreta of benthonic animals. In addition to the redistributed Ba that may persist as barite, Ba is adsorbed to a marked degree by clays, zeolites, and the iron and manganese oxides.

The Ba/Ca ratios of the clams and snails analyzed by Turekian and Armstrong (see table 4) are about 200 times the corresponding ratio in sea water. These authors also noted a marked increase in the Ba content of fossil clam shells compared with those of Recent age.

Many species of the Xenophyophora, a group of marine deep-water rhizopod foraminifera found along the equator and off Ceylon, contain inclusions of BaSO_4 up to 3μ in diameter in their skeletal protein (Schulze and Thierfelder, 1905). BaSO_4 concretions (Jones, 1888; Bøggild, 1912) occur off Ceylon in the same region in which the Xenophyophora are found. However, these relatively uncommon BaSO_4 -forming foraminifera are clearly of minor importance in explaining Ba distribution in sedimentary rocks.

See also tables 1, 19, 23, 26, 27, 28, 30, and 31.

Beryllium

The Be content of five calcareous deep-sea deposits examined by Tatsumoto and Osawa (1957) averaged about 2 ppm, and generally was proportional to the amount of Al present, as shown below.

Percent CaCO_3	53.27	56.59	68.75	80.23	91.13
Be, ppm	4.2	3.1	2.1	1.0	0.5
Percent Al	2.80	3.18	2.67	1.76	0.3

Pieruccini (1944) reported 2.8 to 7 ppm BeO (1 to 2.5 ppm Be) in sedimentary rocks from the Tuscan Apennines. Carbonate rocks fell at the lower end of the range, and the CaCO_3 -free fraction in general contained about 10 ppm BeO (3.5 ppm Be).

Boron

Although the B content of the insoluble residues of the marine and freshwater limestones examined by Degens et al. (1958) are not significantly different (table 5), values for the $<2\mu$ fractions of the insolubles of these materials fall into two non-overlapping groups. The higher B content for the marine samples is attributed ultimately to the greater abundance of B in the ocean. Most of the B in these limestones is in a relatively insoluble form, which in one sample was shown by X-ray diffraction to be tourmaline. Goldschmidt and Peters' finding (1932) that the B content of clay minerals crystallizing in the marine environment is approximately two orders of magnitude greater than the value for terrestrial clays is clearly revelant here. Goldberg and Arrhenius (1958) concluded from various dissolution experiments on Pacific pelagic sediments that some of the B occurred in the structure of the ferromanganese oxide minerals, but that the larger part, which resisted dissolution on boiling in 0.1 N HCl, must proxy for Si in the tetrahedral sheets of clay minerals.

Other studies of marine clay sediments (Landergrén, 1945, 1948; Ernst et al., 1958; Harder, 1958) showed that B content is directly proportional to the salinity of the environment of deposition, inversely proportional to particle size, probably independent of geologic age, and changed in amount by incipient metamorphism but probably not by diagenesis or weathering.

Heide and Thiele (1958) found that B varied from 2.8 to 49.9 ppm (average, 15.4 ppm) in 12 limestones from a Muschelkalk section. Swiss marls containing 65.3, 59.6, 52.8, 49.5, and 44.6 percent CaCO_3 had 26, 33, 43, 47, and 63 ppm B (Hasler, 1942). The average of Hasler's values for purer limestones, cited by Heide and Thiele, is 11 ppm. A fresh-water and a marine dolomite of Carboniferous age contained 0.009 and 0.016 percent B_2O_3 (14 and 25 ppm B) (Ernst et al., 1958), and *Globigerina* oozes from the Pacific Ocean examined by Krasintseva and Shishkina (1959) contained 15 ppm.

The B content of three samples of siderite from the Liassic of southern Sweden (Palmqvist, 1935) ranged from 30 to 160 ppm.

Goldschmidt et al. (1948) reported 0.050 percent B_2O_3 in a bituminous marl of Triassic age from Schröfeln near Wallgau. The *Globigerina* oozes of the *Challenger* expedition contained 0.05 percent B (Goldschmidt and Peters, 1932). Goldschmidt and Peters found 0.01 percent B_2O_3 in the skeleton of *Echinus esculentus*, from 0.0003 to 0.015 percent (average 0.008 percent) B in the skeletal material of four species of Octocorallia, and from 0.003 to 0.03 percent B (average 0.018 percent) in the skeletal material of six species of Hexacorallia. There was 0.01 percent B_2O_3 in the ash from shells of the brachiopods *Lingula anatina* and *Terebratula vitrea*. The shells of *Nautilus pompilius*, *Spirula peronii*, and *Pinna squamosa*, all mollusks, contained, respectively, 0.000545, 0.00027, and 0.00027 percent B.

See also tables 1, 19, 23, 26, 27, 28, 30, 33, and 34.

Bromine and Iodine

The I and Br content in limestones and dolomites depends upon the kind and amount of organic matter in the rock (Correns, 1956). The Br content of the samples listed in table 6 shows no parallelism with Cl, and the amount of Br and I present in iron ores, for example, is proportional to the amount of organic matter present. Itkina (1956) noted that rocks of Carboniferous age from the Saratov-Near Volga region, richer in organic matter than those from the Vereisk horizon, had higher I and Br contents, 9.8 ppm and 16.2 ppm respectively, compared with average values of 6.1 and 10.4 for the Vereisk horizon (see table 6 for average values of Br and I for limestones only). Organic matter and Br are related in the Devonian deposits of the Kuibyshev area, organic matter and I less definitely (Itkina, 1958). Part of the Br and I may be leached with water and part with HCl, but a further portion is apparently bound with organic matter.

Iodine is combined with organic matter in the skeletal parts of Alcyonaria, and ranges from a trace to more than 7 percent of dry weight in the collected analyses presented by Vinogradov (1953). In these analyses Br reaches a maximum value of 4.2 percent of dry weight. Vinogradov's compilation of I determinations made on molluscan shells shows five values for freshwater lamellibranchs with a range of 0.02 to 0.49 mg I per 100 g (average 0.25), 19 values for marine lamellibranchs with a range of 0.02 to 12 mg I per 100 g (average 1.65), seven values for gastropods with a range from 0.024 to 2.40 mg I per 100 g (average 0.64), and values of 0.045 and 0.02 mg I per 100 g for two cephalopods.

Cadmium

Three *Globigerina* oozes examined by Mullin and Riley (1956) contained 0.459, 0.275, and 0.516 ppm Cd, a marine calcareous ooze had 0.574 ppm, and fine-grained drewite sediment from the Bahamas contained 0.124 ppm. The shells of eight present-day marine mollusks gave values from 0.001 to 0.082 ppm Cd (average 0.025 ppm), whereas aragonite precipitated from sea water in the laboratory contains up to 1 ppm Cd. The biological mechanisms involved in shell formation are apparently much more specific in accepting Ca and rejecting Cd than is inorganic precipitation.

See also table 22.

Chlorine

The Cl content of limestones and dolomites occurs principally in liquid inclusions and substituted in the hydroxyl positions of accessory minerals such as hornblende, the micas, and the clay minerals. Apatite generally is present in insufficient amount for its Cl content to be significant (Behne, 1953), and actual grains of minerals such as halite have been reported only in carbonate rocks from evaporite sequences. Clarke (1924) gave values of 0.01 and 0.02 percent Cl for two averaged analyses of 345 and 498 limestones. More recent determinations are summarized in table 6.

The Cl in materials such as the chalk from Rügen and the branched coral, from which most or all of it is water-leachable, must be present in inclusions of sea water (Behne, 1953). Lamar and Shrode (1953) found that more Cl could be water-leached from Illinois dolomites of Paleozoic age than from limestones, but that the reverse was true for water-leachable sulfate. They reported that visible liquid inclusions in the dolomites were smaller but more numerous than those in the limestones. This fact probably explains the difficulty experienced by Behne in water-leaching Cl from the fluorite-bearing Zechstein dolomite, even though

the rock contains only 0.03 percent P_2O_5 and all the Cl is soluble in heated 2N nitric or acetic acid. Graf (1952) checked the extent of soluble-salt extraction from dolomite by its effect upon dolomite thermal decomposition and found the extraction to be a function of the severity of grinding.

The calcareous freshwater tufa of Recent age from Lenglern, near Göttingen, contains only 20 ppm Cl. However, conclusions as to relative salinities of waters in which the various marine carbonates were formed would appear to be premature in the absence of measurements of the actual volumes of liquid inclusion fluids contained in the various specimens.

See also table 31.

Chromium

Six limestones of Ordovician age from Sweden, unmetamorphosed or only slightly metamorphosed, all had either 4 or 5 ppm Cr, except for one sample with 25 ppm that contained local enrichments in Fe believed to have resulted from ancient surface weathering (Lundegårdh, 1949). Katchenkov and Flegontova (1955) reported 0.004, 0.007, 0.006, 0.005, and 0.001 percent Cr for five of the six argillaceous limestones of Devonian age from the Ural-Volga area which they examined. Carbonate rocks from South Lapland examined by Sahama (1945) contained 2 ppm Cr, and Landergren (1948) found 20 ppm in marine siderite ores.

An aragonite-magnesite assemblage from Lake Bonneville sediments, Utah (Graf et al., 1959; unpublished data), contained 11 ppm Cr, and three samples of dolomite sediment contained 11, 12, and 11 ppm. The average Cr content of samples from eupelagic Atlantic core A180-76, containing on the average 78 percent $CaCO_3$, Turekian and Feely (1956) found to be 11 ppm.

See also tables 1, 19, 22, 23, 26, 28, 30, 35, and 36.

Cobalt

Extensive analyses of limestones from New Zealand (table 7) show that in a number of stratigraphic sections exposed in quarries (Willett, 1950) the Co content increases as the limestones become more impure. No correlation appears to exist between Co content and geologic age (Stanton, 1944). Maunsell (1945) attributed the high Co values for limestones of Eocene age from North Island to their nearness to ultrabasic rocks that probably supplied high-cobalt detrital material. He applied the same explanation to Stanton's high Co values for Southland limestones. The Co from these rocks that is soluble in dilute HCl ranges from 13 to 62 percent of the total Co present. Cobalt contents of 11.4 to 26.6 ppm in soils overlying limestones with an average of 4 ppm Co (Dixon and Kidson, 1940) indicate that a fair proportion of the cobalt-bearing compounds are less soluble than limestone in weathering processes. Maunsell pointed out that the analytical method used by Dixon and Kidson gives somewhat low values for specimens rich in silica, which are those containing the most Co.

Malyuga (1949) reported 0.00066, 0.0015, 0.00165, and 0.0015 percent Co in four samples of calcareous sediment from the deeper parts of the Black Sea. Young (1957) noted that Co is found in concentrations of manganese oxide in chert or quartz portions concentrated from originally calcareous rock by weathering.

See also tables 3, 19, 22, 31, 33, 34, 35, 36, and 37.

Copper

Robertson found (Winslow and Robertson, 1894) from 4.0 to 25.6 ppm Cu in six dolomitic limestones of Silurian age from Missouri, the average being 12.6 ppm. Seven Missouri limestones of Lower Carboniferous age ranged from a trace to 88.0

ppm, with an average of 20.2 ppm. Heide and Singer (1950) found an average of 5 ppm Cu in nearly pure carbonate rocks from the Muschelkalk and Röt near Jena. In marly clays as well as in carbonate rocks from this area, the Cu/Zn ratio was nearly 1.

Engel and Engel (1956) made 50 analyses of the Leadville Limestone of Mississippian age near ore at Gilman and Leadville, Colorado, and 75 analyses of the unaltered limestone from localities distributed over 5000 square miles. The Cu content of the samples varied but little from 3 ppm. Analyses of composites of 16 German limestones of Cretaceous age, 45 German limestones of Jurassic age, and 32 German limestones of Devonian age (Wedepohl, 1955) gave 2.1, 1.1, and 1.6 ppm Cu, respectively. Two limestones examined by Higazy (1954) contained 4 and 6 ppm Cu, and four unmetamorphosed Mississippian age limestones from the Hanover District, New Mexico, had 8, 17, 35, and 0 ppm (Barnes, 1959).

Shells of *Arca* from Gaybu-Pernambuco beach contained 1.8 ppm Cu, *Spirula* from Praia Granda, St. Vincent, 2 ppm, a sea urchin test from Bahia beach, 25 ppm, and calcareous algal material from San Carlos, Fernando Po, 1.5 ppm Cu (Wedepohl, 1955).

Itkina (1948) gave values of 0.0006, 0.00038, 0.0014, and 0.00119 percent Cu (average 0.00089 percent) for bituminous limestones of Carboniferous age from the Ural-Volga region. Gulyaeva and Itkina (1950) found 0.00624 and 0.00542 percent Cu in two limestones of Upper Permian age from the Tatar A.S.S.R., and 0.02888 and 0.026 percent Cu in two dolomites. Katchenkov and Flegontova (1955) found 0.006, 0.02, 0.011, 0.002, and 0.00035 percent Cu in five of the six argillaceous limestones of Devonian age from the Volga-Ural area they examined. Carobbi and Pieruccini (1943) reported 7.2 ppm Cu in a limestone containing 13.71 percent SiO_2 , 1.79 percent Al_2O_3 , 0.17 percent P_2O_5 , 2.75 percent Fe_2O_3 , 2.33 percent FeO , 0.15 percent Na_2O , 1.34 percent K_2O , 0.93 percent MgO , and 0.47 percent MnO .

Malyuga (1949) found 0.005, 0.011, 0.0045, and 0.0056 percent Cu in four samples of calcareous sediment from the deeper parts of the Black Sea. The average Cu content of samples from eupelagic Atlantic core A180-76, containing on the average 78 percent CaCO_3 , was found by Turekian and Feely (1956) to be 18 ppm.

See also tables 1, 3, 22, 24, 26, 27, 28, 29, 30, 31, 32, 33, 34, and 37.

Fluorine

Much of the relatively small amount of F in carbonate rocks is substituted in apatite grains, in the phosphates making up bones, teeth and brachiopod shells, and in micas, clays, and hornblende (Koritnig, 1951; Correns, 1957). The bones of four freshwater fish analyzed by Vinogradov (1953), for example, contained from 0.022 to 0.043 percent F (average 0.034 percent); those of nine marine species contained from 0.043 to 1.08 percent F (average 0.43 percent). The ratio between these two averages is about that for the concentrations of F in fresh and marine waters. Bones and authigenic phosphates continue to increase their F content by reaction with the surrounding aqueous medium. Thus, horse bones of Recent age contain only 0.01 to 0.03 percent F, but those of Miocene age from Florida have F contents that group around 1.7 and 2.6 percent F (Olsen, 1950). In a number of instances where the content of minerals containing substituted F is inadequate to account for all the F in carbonate rocks, the presence of small amounts of fluorite has been verified by careful examination.

Correns (1956) pointed out that the Zechstein age reef limestone of table 6 contains crystals of fluorite even though it has a low F content, and that F in such cases may have migrated within the sediment after solution of one of the fluorine-

bearing host minerals. Although small crystals of fluorite have been reported in the Tennessee phosphates, the crystals described by Whitlatch and Smith (1940) from phosphatic limestones there are not always in the areas of phosphate minerals, which also suggests local transport and redeposition.

Scattered fluorite crystals have been noted in limestone quarries south of East St. Louis, Illinois (Schrout, 1950). Thin veinlets of fluorspar occur in the chert nodules of a limestone bed in a quarry near Anna, Illinois (J. E. Lamar, personal communication). A small but more extensive vein of fluorite also was found in the same quarry. The hydrothermal fluorite-sulfide mineralization of Hardin County, Illinois, is only about 50 miles from Anna but about 120 miles from the East St. Louis quarries.

Two occurrences of sellaite, MgF_2 , in bituminous anhydrite-bearing dolomites at the Gebrouloz Glacier in Savoy and at Bleicherode am Harz (Koritnig, 1951; Correns, 1956) are believed by Correns, because of the high solubility of MgF_2 , to be secondary alteration products of CaF_2 .

A relation between fluorite deposition and algal remains is suggested by two occurrences, both of which are in evaporite sequences. Fluorite is found in the Magnesian Limestone of Durham, England, and in algal structures (*Filograna permiana*) from the Aislaby boring (see discussion after paper by Raymond, 1953). It also occurs in insoluble residues from Zechstein Dolomite of Permian age in north Germany that contains algal (?) grains (Koritnig, 1951), and from early Tertiary age limestones of south Germany that are made up of *Lithothamnion* masses (Hans Fuchtbauer, personal communication).

The amounts of fluorite that Kazakov and Sokolova (1950) were able to dissolve in distilled water and in artificial sea water correspond to fluoride ion concentrations roughly ten times those found in comparable waters in nature, indicating that fluorite precipitation could not be expected in these natural environments. With increasing Ca^{++} concentration, the experimentally determined solubility of fluorite decreases because of the common ion effect; on the other hand, increasing the concentration of MgSO_4 increases fluorite solubility, as does an increase of NaCl up to a point. Thus, when sea water is concentrated, these opposing effects are found experimentally to result in a solubility minimum for fluorite, at 3X or 4X initial concentration, of about 4 mg/lF, which is about the same as the F value for sea water concentrated 4X. Calcium carbonate and calcium sulfate precipitate at somewhat greater degrees of concentration, resulting in an increase in the solubility of fluorite through destruction of the common ion effect. Thus, there is a limited concentration range in which the precipitation of fluorite in carbonate sediments might occur. If there were periodic additions of river water to a saline basin, the possibility of fluorite precipitation would be enhanced because of the higher ratio of F to total dissolved solids in river water compared to ocean water.

Kazakov and Sokolova obtained most of their solubility data by immersing fluorite powder in the appropriate solution and determining fluoride content in samples of liquid at intervals until no further increase in fluoride concentration was observed. Some of these experiments took as much as 130 days. The usual doubts as to whether equilibrium actually was reached were partially dispelled by a few experiments with calcium-enriched systems in which the final fluoride concentration in the liquid phase was approached by precipitating fluorite from a supersaturated solution. Satisfactory agreement with the values obtained by solution of fluorite was reached.

As Kazakov and Sokolova pointed out, many of the sedimentary occurrences of fluorite are associated with celestite and restricted to evaporite carbonate and calcium sulfate facies, as would be expected from the experimental results. Conversely, the occurrence of disseminated fluorite in these particular rocks is a

strong argument for its sedimentary origin. Fluorite crystals found in cavities in dolomite of the Niagaran Group at Niagara Falls, Welland County, and elsewhere in southern Ontario (Wilson, 1929) bear no apparent relation to major disturbances. Celestite and fluorite, together with lesser amounts of calcite, anhydrite and gypsum, iron sulfide, and sphalerite line and fill solution cavities in the Guelph Dolomite of the Niagaran Group of Silurian age at Clay Center (Morrison, 1935) and elsewhere in northern Ohio (Fitzgerald and Thomas, 1932). Pustovalov (1937) found that in the cyclic sedimentary rocks of the upper Volga area fluorite was restricted to the dolomitic rocks of each cycle. Yarzhemskij (1955) correlated recrystallization of dolomites in evaporite sequences with silicification and the appearance of sporadic accumulations of fluorite, celestite, and other minerals that he believed were present earlier as finely disseminated particles.

See also tables 19 and 34.

Gallium

Goldschmidt and Peters (1931) found 0.0005 percent Ga_2O_3 in *Globiigerina* ooze from *Challenger* station 332, and reported that amount or less in numerous Mesozoic age limestones studied. Shaw (1957) noted that carbonate rocks are very poor in Ga, like most other nonaluminous sedimentary rocks, and gave 4 ppm as a probable average. An aragonite-magnesite assemblage from Lake Bonneville sediments, Utah (Graf et al., 1959; unpublished data), contained 3 ppm Ga, and three samples of dolomite sediment showed 3, 4, and 2 ppm.

The average difference between the Ga content of the $<2\mu$ fractions of the insoluble residues of freshwater and marine limestones examined by Degens et al. (1958) is significant at the 5 percent level, and also is clearly evident for the complete insoluble residues (see table 5). The higher Ga content of the freshwater limestone is attributed ultimately to the greater abundance of Ga in fresh waters. The Ga must be combined in a relatively insoluble form, probably in the clays.

Goldberg and Arrhenius (1958) were unable to detect Ga in two foraminiferal oozes, but found 13 ppm in a *Globiigerina* ooze (34 ppm in the residue after removal of carbonate by acid). The Ga contents found by Burton et al. (1959) for some of the samples described below in the germanium section are 17.7 and 3.7 ppm in *Globiigerina* oozes, 6.5, 8.5, and 5.7 ppm in deep-sea calcareous clays, 0.06 ppm in drewite, 0.02 to 0.30 (average 0.10 ppm) in eight limestones, chalks, and calcites from limestones, 0.07 ppm in a dolomite, 0.8 and 0.04 ppm in two siderites. Culkin and Riley (1958) measured about 0.1 ppm Ga in mollusk shells. The average proposed by Burton et al. for carbonate rocks, 0.06 ppm, is from one-fortieth to one-seventieth of Shaw's estimate, the few values by Graf et al., and the average value of 2.2 ± 1.2 ppm for Scottish rocks (Geol. Survey Great Britain, 1956; see table 19). Considering the *Globiigerina* ooze values of Burton et al. and the fact that their limestone samples are clay-poor types (chalks, oolites, calcite concentrates), an estimate of about 2.5 ppm would seem closer to a true over-all average for sedimentary carbonate rocks.

See also table 5.

Germanium

El Wardani (1957) reported 0.0 ppm Ge in four samples of *Globiigerina* ooze, three dolomites, and a limestone, using spectrophotometric determination of Ge as the phenylfluorone-germanium complex.

Burton et al. (1959), using the same method as El Wardani, found from 0.14 to 0.41 ppm Ge (average 0.25 ppm) in seven mollusk shells. Three deep-sea calcareous clays containing from 54.5 to 60.2 percent CaCO_3 plus MgCO_3 had 1.0,

1.0, and 0.9 ppm Ge, a pteropod ooze containing 73.5 percent carbonates showed 0.6 ppm, a *Globigerina* ooze with 92.6 percent carbonates had 0.0 ppm, and another *Globigerina* ooze contained 1.4 ppm. A sample of fine-grained aragonite sediment (drewite) from the Bahamas contained 0.04 ppm Ge, eight limestones, chalks, and calcites from limestones had 0.03 to 0.10 (average 0.07 ppm), a dolomite showed 0.17 ppm, and two siderites contained 0.12 and 0.45 ppm. Ge in the calcareous oozes and muds is found entirely in the clay minerals. Burton et al. gave 0.09 ppm as an average Ge content for carbonate rocks.

See also table 22.

Gold

Wagoner (quoted in Clarke, 1924) found 0.005 and 0.0086 ppm Au in two marbles from California and Carrara, Italy.

See also table 22.

Indium

Shaw (1952), using a double-arc spectrochemical method, was unable to detect any In in a limestone, a dolomite, and a sample of *Globigerina* ooze. Nor was Erämetsä (1938) able to detect In in 15 Finnish carbonates. Goldschmidt (1937) noted a concentration of In in sedimentary and hydrothermal siderite rocks.

Lead

Wedepohl (1956) gave an average value of 0.0009 percent Pb in limestones (table 8) and stated that the value for dolomite is of the same order of magnitude. The insoluble residue of Wedepohl's samples, averaging 10 percent of the rock, contained about a third of the total Pb. This is not surprising, for he commented that most of the Pb in sediments occurs in clays. It is also worth noting that bituminous Malmkalke from Süntel, Lower Saxony, has more than twice as much Pb in the bituminous part as in the nonbituminous, and that the flint of the Cretaceous of Sylt contains more than 0.0020 percent Pb. It thus appears that the bituminous and siliceous portions of the insoluble residues may carry Pb at a concentration above that of the carbonate host.

Although Wedepohl said pure biogenic calcites normally contain no more than 0.0001 percent Pb, he found that the foraminifera in deep-sea oozes contain an average of 0.016 percent Pb, the mechanism of fixation being unknown. The living matter of Echinodermata was similarly cited as containing up to 0.0021 percent Pb, whereas that of jellyfish contains some 0.0027 percent. It is thus possible that some of the Pb fixed in biogenic carbonate rocks may have passed through an earlier stage of biogenic concentration.

Patterson et al. (1953) found 0.31 ppm Pb in the dilute-acid-soluble fraction of a sample of Lomita Marl of Pleistocene age from southern California that contained 1.5 percent insoluble residue. The Pb composition, as atomic ratios with an assigned absolute error of 1 percent, is $Pb^{206}/Pb^{204} = 19.27$, $Pb^{207}/Pb^{204} = 15.61$, $Pb^{208}/Pb^{204} = 39.40$. The differences between these ratios and the somewhat lower ones observed for red clay and a manganese nodule may stem from the near offshore depositional environment of the marl or from nonrepresentative Pb contributions from the insoluble residues.

The Mississippian age Leadville Limestone of Colorado contains 1.9 ppm Pb and 0.4 ppm U, with $Pb^{206}/Pb^{204} = 21.23$, $Pb^{207}/Pb^{204} = 15.83$, and $Pb^{208}/Pb^{204} = 39.33$ (Engel and Patterson, 1957). The U present is insufficient to sup-

port the radiogenic Pb, and it is supposed that a separation of Pb and U took place during sedimentation.

See also tables 1, 19, 22, 26, 27, 28, 29, 30, and 32.

Manganese

The average Mn content of 293 composite carbonate samples (10,389 specimens) from the post-Proterozoic rocks of the Russian Platform is 530 ppm (Ronov and Ermishkina, 1959), compared with 490 ppm for sands and silts and 580 ppm for clays. Ronov and Ermishkina made a distinction between carbonate rocks formed in humid and arid climates, because of the importance in weathering of waters rich in organic acids. The average Mn content of 3967 carbonate rocks believed to have been produced in a humid climate is 810 ppm, whereas that of 6422 samples from arid climates is 320 ppm. The amount of Mn in these samples correlates well with the amounts of Fe and of insoluble residue. However, the average value of

$$\frac{\text{MnO}}{\text{FeO} + \text{Fe}_2\text{O}_3}$$

for the carbonate rocks is 0.040, compared with a range from 0.011 to 0.024 for clays, sands and silts, and various igneous rock types, indicating some geochemical separation of Mn and Fe in zones of carbonate sediment accumulation.

Investigations of possible source rocks for supergene Mn oxide deposits formed by weathering and chemical concentration at various localities in the United States have yielded some data on above average Mn contents in sedimentary carbonate rocks. Seven analyses of the upper and lower parts of the Shady Dolomite of early Cambrian age showed 0.15 to 0.87 percent Mn, and the "ribboned member" had 1.24 percent (King et al., 1944). The Shady Dolomite encountered in a drill core at Bumpass Cove, Tennessee, contained an average of 0.46 percent Mn (Rodgers, 1945). The average soluble Mn content of 15 samples of the Mount Athos Formation was 0.39 percent (Espenshade, 1954). The Fernvale Limestone of the Lower Ordovician in the Batesville district of Arkansas contains from 0.01 to 3 percent Mn (Miser, 1922). The limestone with which small, widely distributed deposits of Mn oxide are associated in southeast Utah contains 0.02 to 0.48 percent Mn (Baker et al., 1952).

An aragonite-magnesite assemblage from Lake Bonneville sediments, Utah (Graf et al., 1959; unpublished data), contained 250 ppm Mn, and three samples of dolomite sediment had 320, 350, and 250 ppm. The Mn content of seven samples of limy silt from the Black Sea was 0.04 to 0.05 percent (Strakhov, 1947). Fourteen samples of these limy silts contained from 50.37 percent to 72.47 percent CaCO_3 (average 58.7 percent). Five samples of sediment from the western shelf of the Caspian Sea, containing from 14.3 to 17.6 percent material insoluble in 10 percent HCl (average, 15.7 percent) and from 71.8 to 78.5 percent CaCO_3 (average 75.4 percent) as calculated from determined CO_2 , had from 0.018 to 0.020 percent Mn extractable in 10 percent HCl (average 0.019 percent). Fourteen other samples from various localities in the Caspian Sea had 50.2 to 67.3 percent (average 56.6 percent) calculated CaCO_3 , 23.6 to 41.8 percent (average 32.6 percent) material insoluble in 10 percent HCl, and 0.018 to 0.089 percent (average 0.042 percent) Mn. Of these 14 samples, the six from the section Kurinski Kamen Island — Ogurchinski Island contained from 0.044 to 0.089 percent extractable Mn (average 0.062 percent), although their average calculated CaCO_3 content of 57.7 percent is essentially identical with that of the other samples (Bruevich, 1946).

Correns (1928) reported that Mn varied directly with CaCO_3 in the *Meteor* samples, but in the North Atlantic cores (Bramlette and Bradley, 1940) the two were found to be independent. Wangersky (1959) found that Mn in two cores from the equatorial portion of the mid-Atlantic Ridge reached very high concentrations in the zone from about 13 to 27 cm depth, and suggested that originally deposited MnO_2 is converted on burial to a more soluble manganous salt and expressed up the sediment column to a layer of re-oxidation and redeposition.

Samples taken throughout the predominantly CaCO_3 core A179-4 from latitude $16^\circ 36' \text{ N}$, longitude $74^\circ 48' \text{ W}$, contain between about 0.09 percent and about 0.024 percent Mn (percent of dry sediment). No correlation exists between Mn and either Ca or the major constituents Si, Al, Fe, and Ti, but an irregular inverse relation with a highly significant correlation coefficient (-0.511) exists (Wangersky and Hutchinson, 1958) between the percentage of Mn and the surface temperatures determined by Emiliani (1955a, 1957) using $\text{O}^{18}/\text{O}^{16}$ paleothermometry.

Sedimentary siderites from Scania, Sweden, (Palmqvist, 1935, recalculated by Landergren, 1948) contained 2800 ppm Mn, and marine siderite ores examined by Landergren had 2600 ppm Mn.

Marcelet (1913) stated that the dry matter of Corallinaceae, of which about half is ash residue, chiefly CaCO_3 , contains up to 0.02 percent Mn. A modern *Lingula anatina* from Ceylon consisted of 52.10 percent organic matter and 47.90 percent ash, the latter containing 0.46 percent Mn_3O_4 (Vinogradov, 1953). Ten shells of lamellibranchs contained from 0.001 to 0.078 percent Mn in the ash (average 0.037 percent), and those of three gastropods had 0.001, 0.005, and 0.002 percent Mn (Vinogradov, 1938).

Correns (1941) suggested a biological extraction of Mn from sea water into foraminiferal tests, followed by partial dissolution and release of some Mn^{++} into pore water of the surface layer of the sediment. Analyses, by G.O.S. Arrhenius and his co-workers, of planktonic foraminifera (see Goldberg and Arrhenius, 1958) appear to bear this out.

See also tables 22, 23, 25, 26, 27, 28, 29, 30, 32, 33, 34, 35, and 37.

Mercury

Stock and Cucuel (1934) distilled 3.3 micrograms/100 g (0.033 ppm) of Hg from a sample of Muschelkalk from Baden. Heide and Bohm (1957), using the same method, found from 0.028 to 0.1 ppm Hg (average 0.048 ppm) in 12 highly pure Muschelkalk samples. Values for clayey members of the Röt were four times as high. Fluctuations in Hg content among the Muschelkalk samples paralleled those of Zn and Cu.

Molybdenum

The Mo contents of 12 limestones and dolomites from the United States, determined by the colorimetric molybdenum thiocyanate method, ranged from 0.1 to 1.2 ppm with an average of 0.4 ppm (Kuroda and Sandell, 1954). Average values for dolomites and for limestones are the same. Carbonate rocks containing organic matter may be enriched in Mo. The highest value found was 1.2 ppm, the only one above 0.5 ppm, and is for a carbonaceous limestone from Greene County, Pennsylvania. A sample of *Globigerina* ooze from the Pacific Ocean contained 3 ppm Mo (Kuroda, 1942).

See also tables 22, 25, 26, 28, 30, 34, and 37.

Nickel

A very pure limestone from a bore hole at Key West, Florida, containing only 0.07 percent SiO_2 and 0.16 percent $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, had 0.0009 percent Ni. A composite of 19 samples of limestone from 18 states and one foreign country contained 0.0011 percent Ni (Wells, 1943). The average Ni contents of the 0 to 25, 30 to 260, and 265 to 410 cm portions of calcareous eupelagic Atlantic core A180-76 were 13, 17, and 13 ppm (Turekian, 1958). Lundegårdh (1949) found that six limestones of Ordovician age from Sweden, unmetamorphosed or slightly metamorphosed, contained from 2 to 90 ppm Ni, with an average of 19 ppm. If the sample containing 90 ppm Ni, which has local enrichments in Fe believed to have resulted from ancient surface weathering, is ignored, the range is 2 to 10 ppm and the average 5 ppm. Katchenkov and Flegontova (1955) reported 0.005, 0.0053, 0.006, 0.001, and 0.001 percent Ni for five of the six argillaceous limestones of Devonian age from the Volga-Ural area they examined. Gulyaeva and Itkina (1950) found 0.002 percent Ni in a limestone of Upper Pennsylvanian age and 0.00142 percent Ni in a dolomite from the Tatar A.S.S.R.

An aragonite-magnesite assemblage from Lake Bonneville sediments, Utah (Graf et al., 1959; unpublished data), contained 6 ppm Ni, and three samples of dolomite sediment contained 4, 6, and 3 ppm.

Malyuga (1949) determined 0.0023, 0.0054, 0.0034, and 0.0032 percent Ni in four samples of calcareous sediment from the deeper parts of the Black Sea. A few lime-rich *Albatross* cores analyzed by Mag. Bauer for Ni (Pettersson and Rotschi, 1952) contained only a few parts per hundred thousand. The contents of Ni and Fe in the cores, calculated on a noncalcareous basis, are about the same as in red clay.

Marine siderite ores examined by Landergren (1948) contained 50 ppm Ni.

See also tables 1, 3, 19, 22, 24, 25, 26, 28, 29, 30, 31, 35, 36, and 37.

Radium, Uranium, and Thorium

Sedimentary apatite contains from 50 to 300 ppm U, typically about 100 ppm, and in many limestones is the major host for U (Clarke and Altschuler, 1958). On the basis of ionic size, the U substituted for Ca in apatite should be U^{+4} , and Clarke and Altschuler found that U^{+4} makes up a higher percentage of the total U in young and unweathered material, indicating that initially fixed U^{+4} is oxidized to U^{+6} during weathering. Surface concentrations of U observed on sedimentary apatite (see Bowie and Atkin, 1956) have been shown by Neuman et al. (1949a) to result from adsorbed uranyl ions, UO_2^{++} , displacing two Ca ions per uranyl ion.

The extremely low syngenetic U content of typical carbonate sediments and rocks is explained by the high bicarbonate ion concentrations and the oxidizing nature of the environment in which they are typically deposited (Bell, 1956). In solutions containing carbonate and bicarbonate ions, the oxidized uranyl ion forms a relatively undissociated tricarbonic complex that may be transported long distances unless reducing conditions or an environment of lowered pCO_2 such as the surface is reached (Gruner, 1956). Thorium has no comparable oxidized state in such environments and so remains in the insoluble detrital fraction or is precipitated as a hydrolysate and is separated from U.

Tetravalent U also forms a carbonate complex (McClaine et al., 1956). Sheldon (1959) gave a critical review of the mechanisms involved in U transport and deposition in environments of varying pH and Eh.

It can be argued that phosphatic, carbonaceous, and argillaceous limestones should not contain a great deal more adsorbed U than nearly pure carbonate rocks,

because adsorption on clays, organic matter, and phosphates would have been inhibited by the ionic composition of the solution. Uranium adsorption by replacement of surface Ca atoms of phosphates is found experimentally to be drastically reduced with moderate increases of Ca and bicarbonate ion in solution, because of the increased Ca competition for surface cation sites and because of the uranyl ion complexing with carbonate in solution (Neuman et al., 1949b). The reduced U adsorption observed at elevated pH may be considered in part the result of competition between surface phosphate groups and hydroxyl ions. The U content of phosphorites and black shales drops sharply with the advent of only a few percent carbonate (McKelvey and Nelson, 1950). Phosphatic nodules in limestone and residual concentrates of phosphate from such limestone are in fact generally nonuraniferous, and limestones phosphatized by the leaching of guano deposits contain less than 0.01 percent U (Davidson and Atkin, 1953; McKelvey and Nelson, 1950). In general, few samples that contain more than 0.01 percent U also contain more than 3 or 4 percent CO_2 (Page et al., 1956); the decrease in U with decrease in CO_2 is greater than would result from mere dilution.

Much of the nonphosphate U found in carbonate rocks appears to have been redistributed by ground water and in some instances by petroliferous fluids. Solid asphaltic residues coat fractures and stylolites and are distributed randomly as pellets in the dolomites of early Permian age in the Panhandle gas field, Texas, and in dolomites of the gypsiferous Seven Rivers Member of the Chalk Bluff Formation that crops out near Carlsbad, New Mexico (Bell, 1956). In some places the pellets are not uraniferous but in others they contain as much as 1.6 percent U.

According to Hail (1957), crude oil consistently has a very low U content, and the slightly higher amounts of U found in the asphalts of asphaltic limestones can be explained by concentration from loss of the lighter fractions. Anacacho Limestone of Cretaceous age from Texas contained 8.52 percent material extractable with a hot benzene-acetone-methanol mixture, and Viola Limestone of Cretaceous age from Oklahoma contained 3.18 percent. The asphalt of the Anacacho had 0.1 ppm U, and the asphalt of the Viola, 0.07 ppm. However, one of the asphalts from limestone described by Erickson et al. (1954) (see table 24) contained 150 ppm U, and a different mechanism of U concentration must be required for this material.

Small lenses and nodules of chert in thin, freshwater limestone beds of the tuffaceous Browns Park (?) (Miocene) and North Park (?) (Pliocene) (?) Formations of Carbon County, Wyoming, are uraniferous, and U minerals variously reported as uranophane and carnotite coat fractures and vugs and are disseminated through the limestone. Both the silica and the U are believed to have been leached from interbedded vitreous volcanic sediments by ground water during conversion of these sediments to bentonitic clays. A similar history is postulated for the U found in thin limestone beds in the upper part of the Green River Formation near Myton, Utah (Love, 1953; Bell, 1956; Gabelman, 1956; Stephens and Bergin, 1959). Local concentrations of U at the Wyoming locality reach 1500 ppm, and those at the Utah locality reach 180 ppm.

Mobility of U in the weathering zone is indicated by the disequilibrium of U and its decay products in the topmost foot of the limestone at the Miller Hill area, Carbon County, Wyoming, where radiometrically determined U is always higher than chemically determined U (Vine and Pritchard, 1959). Equilibrium is more nearly approached in the lower part of the limestone.

Secondary U minerals fill cavities in marine limestones as in any other rock type, but replacement is generally not significant (Gabelman, 1956). However,

metatyuyamunite replaces both cement and oolites adjacent to fractures in oolitic limestone in Johnson County, Wyoming (Guilinger and Theobald, 1957); the rock contains from 0.017 to 0.32 percent U and from 0.06 to 0.17 percent V_2O_5 .

Tufa and travertine deposited by springs in the Split Rock area, Fremont and Natrona Counties, Wyoming, contain up to 180 ppm U, thought to have been deposited principally because of evaporation (Bell, 1956). Carnotite, tyuyamunite, and manganese oxides coat limestone boulders in caliche and largely fill joints and bedding planes of the Hueco Limestone of Permian age in El Paso and Hudspeth Counties, Texas.

The radiometrically determined Th and U contents of composites of several thousand carbonate rock samples from the Russian Platform (Baranov et al., 1956) are given in table 9. The bulk of the Th occurs in the insoluble residue, as shown by the correlation between high Th values and high insoluble residue percentages. High Th concentrations correspond to periods when the carbonate sediments were receiving increased amounts of terrigenous detritus. U, on the contrary, is transported in solution and its concentration is thus more nearly constant in these samples. Baranov et al. noted some U enrichment in carbonate samples high in organic matter.

Adams and Weaver (1958) determined U fluorimetrically, made total alpha counts, and used a scintillation counter to discriminate between the 1.76 Mev gamma rays from the U series, 1.47 Mev from K^{40} , and 2.62 Mev from the Th series. The U, Th, and Th/U values obtained indicate that fairly well consolidated, unweathered sedimentary rocks that do not have large amounts of pore water that can dissolve oxygen and emanation will be in secular radioactive equilibrium. The results given in table 10 incorporate earlier determinations made by Evans and Goodman (1941) and Breger (1955) using the emanation method and cited by Adams and Weaver. There is a generally good correlation between the percentage of insoluble residue and the percentage of Th, in spite of the fact that some residues consist of low-thorium anhydrite and chert. The Russian Platform samples have a higher average Th content but also a higher insoluble residue content than the North American samples. A positive correlation exists between Zr and Th in eight of Adams and Weaver's samples for which Zr was determined.

The percentage of total U found in the acid-soluble fractions ranges from 50 to 80 in these samples, averaging close to 80 percent. There is a fair correlation between ppm U in the insoluble residue and the percentage of insoluble residue, indicating a typical U content of about 4.5 ppm in the insoluble fraction. Essentially none of the U contained in accessory illite and only about 10 percent of that in montmorillonite is leached during the acid treatment, judging from analogous acid-leaching tests of samples of clays obtained from shales.

The lithogenous contribution of radioactivity is shown to be unimportant in Pacific pelagic sediments by the fact that most of the ionium (Th^{230}) is not U-supported (see Arrhenius and Goldberg, 1955). Furthermore, the contribution of radioelements by biogenic $CaCO_3$ is much less important than that from hydrogenous materials. The shell material in a Pacific mud sample examined by Evans et al. (1938) contained only a small amount of the total Ra content of the sample. Core *Capricorn* 39 BG with some 70 percent $CaCO_3$ had a beta-activity based upon its $CaCO_3$ -free weight that was equivalent to that of adjacent carbonate-free pelagic clays.

The surface water at $124^\circ 41.0' W$, and $33^\circ 54.5' N$, contained five percent or less of the equilibrium amount of ionium, and a sample from a depth of 3500 meters had less than 1 percent (Sackett et al., 1958). The results for the deep-water

sample agree with those Koczy et al. (1957) found for samples of coastal water collected in the Skagerak and Gullmerfjord. Not only ionium but apparently also Pa^{231} or Ac^{227} , or both, are precipitated with the Pacific sediments, for the Th^{227} concentration in the surface and deep-water samples is also below its equilibrium concentration with respect to U^{235} . Suggested scavengers responsible for the concentration of unsupported ionium in the pelagic sediments include ferric hydroxide (Petersson, 1953), manganese oxides (Goldberg, 1954), precipitated aluminosilicates (Arrhenius and Goldberg, 1955), and the microcrystalline apatite of bathypelagic fish debris (Arrhenius et al., 1957).

The $\text{Th}^{230}/\text{Th}^{232}$ ratios of 12 bottom samples from the eastern Pacific analyzed by Goldberg and Koide (1958) fall into two geographical groups having typical ratios of 15 and 35. They believed that the overlying water masses in the two areas will show a similar ratio difference. In 10 of 12 East Pacific cores, the ratio $\text{Th}^{230}/\text{Th}^{232}$ decreases exponentially with depth.

Coral limestone core samples taken from depths down to 200 feet from Eniwetok Atoll have been analyzed for U fluorimetrically and for ionium by thenoyltrifluoroacetone extraction of total Th followed by pulse analysis of alpha-activity in the separated Th (Barnes et al., 1955, 1956; Sackett, 1958). Uranium in core F-1 varies between 2.9 and 5.5 ppm, with an average of 3.95 ppm; in core E-1, U varies from 0.64 to 3.92 ppm, with an average of 2.4 ppm. Ionium is less than 10^{-6} ppm near the surface, reaches (in core E-1) 4×10^{-5} ppm at 100 feet, decreases to 2×10^{-5} ppm, and then increases again to more than 4×10^{-5} ppm at 180 feet. The uranium and ionium reported are the acid-soluble amounts, which are assumed to be essentially total amounts because the acid-insoluble material, mainly silica, is never more than 1 percent of the rock.

Newly deposited coral limestone at Eniwetok contains less than 1 percent of the ionium needed for secular equilibrium. Near-surface limestones contain less than 10 percent of that amount. At 180 to 190 feet in core E-1 the figure is 85 percent, and at 180 to 190 feet in core F-1 it is 108 ± 9 percent. Ionium-poor sea water is left for corals and other CaCO_3 -forming organisms to draw upon after most of the ionium has been coprecipitated elsewhere in pelagic sediments. With continued formation of ionium in the coral limestone as a result of the radioactive decay of U, the equilibrium concentration of ionium is gradually approached.

Sackett found the U content of 11 coral limestone samples consisting principally of aragonite ranged from 1.05 to 3.46 ppm (average 2.4 ppm), whereas eight samples made up of calcite or calcite and dolomite ranged from 0.17 to 0.67 ppm, except for one value of 3.1 ppm (over-all average 0.7 ppm). The large change in U concentration that apparently occurs with recrystallization is not accompanied by a corresponding change in Th concentration. The Th^{232} in 22 assorted core samples ranged from 0.009 to 0.13 ppm (average 0.054 ppm), corresponding to a range of $\text{Th}^{232}/\text{U}^{238}$ ratios from 0.002 to 0.07 (average 0.02). In checking the Th^{228} content of coral limestones, in connection with the use of Th^{228} tracer to determine the yield of the chemical extraction process, a sample from 110 to 120 feet in core F-1 was found to have less than 2.33×10^{-11} ppm Th^{228} .

Sackett pointed out that the U/Ca ratios of most of the aragonitic materials are within plus or minus 20 percent of the atomic ratio of these materials in sea water, obtained using values of 0.40 g/l for Ca and 3.0×10^{-6} g/l for U. However, a biological control is suggested by the low U values for the aragonitic clam *Tridacna* and for the aragonitic algal CaCO_3 in table 11. U/Ca ratios greater than those of sea water are thought to result from the presence of phosphatic fossils or, in porous material such as coral, perhaps from later exchange with ocean water.

Unlike the marine deposits, newly deposited tufa is not ionium-free. Sackett observed an ionium activity of 0.45 disintegrations per minute per gram in a currently forming tufa having a C^{14} age estimated as less than 50 years. This sample also contained more than 100 times the Th^{228} that could be supported by the grandparent Th^{232} . The excess Th^{228} is believed to have grown in from Ra^{228} , which has a half-life of only 6.7 years and was presumably transported in solution by streams to the lake and coprecipitated with the $CaCO_3$.

The Ra content of sea water is only about 10 percent of the amount required for secular equilibrium with the U present (see review in Bernert, 1951), but is far in excess of that which can be supported by the ionium in sea water (Koczy et al., 1957; Sackett et al., 1958). The Ra deficiency relative to U results from the above-discussed precipitation of its parent, ionium. Pettersson (see Bernert, 1951) predicted that the Ra content of deep-sea sediments should build up with depth until it is in radioactive equilibrium with the ionium present and then decrease with the gradual disappearance of ionium until only the small amount of Ra in equilibrium with U remained. Piggott and Urry (1941), Urry (1949), and Bernert (1951) calculated sedimentation rates based upon this model.

The excess of Ra in sea water relative to ionium suggests that Ra originating from ionium in the sediments is being redissolved (Sackett et al., 1958). Arrhenius and Goldberg (1955) showed that redistribution of ionium-supported radium by diffusion through the interstitial solution of the sediments occurred, followed by scavenging by the authigenic zeolite phillipsite.

The concentrations of Ra found in *Globigerina* oozes (see Hamaguti, 1938, 1939; Piggott and Urry, 1939; Kröll, 1955) range from 1.15 to 8.25×10^{-12} g Ra/g. Averaging these values is pointless, because of the variation of Ra concentration with depth in response to ionium and U concentrations.

Of the limestones examined by Bell et al. (1940), the shaly ones contained the most Ra. All of these limestones were over one million years old and the Ra was in radioactive equilibrium with U. The Ra actually found in the Austin and Selma Chalks of Upper Cretaceous age by Breger (1955), when increased by the Ra equivalent of the determined radon loss, deviates at most 11 ± 4 percent from the theoretical Ra for the U found, indicating that the samples are in radioactive equilibrium.

See also tables 12, 22, and 24.

Rare Earths

A sample of Todilto Limestone from sec. 30, T. 13 N., R. 9 W., New Mexico, contained 0.0033 percent total rare earth oxides (Irving Breger, personal communication; Harry Levine and Irving May, analysts). Spectrographic analysis of a chemical concentrate of the rare earths gave, in percentage of the original rock, Y, 0.00130; Ce, 0.00100; La, 0.00060; Nd, 0.00030; Pr, 0.00010; Sc, 0.00002; Sm, 0.00008; Gd, 0.00006; Dy, 0.00004; Ho, 0.00001; Er, 0.00005; Tm, 0.00001; and Yb, 0.00001 percent. The limestone was of high purity, containing only (semi-quantitative estimates) 0.5 to 1.0 percent Si, 0.1 to 0.5 percent Al, 0.1 to 0.5 percent Mg, 0.05 to 0.1 percent Fe, and 0.01 to 0.05 percent Na (C. L. Waring and K. E. Valentine, analysts).

Sahama (1945) reported 0.001 percent La_2O_3 , 0.004 percent CeO_2 , 0.001 percent Y_2O_3 , and 0.0001 percent Sc_2O_3 in a dolomite from southern Finnish Lapland, but it is not clear whether the rock has undergone metamorphism. Eberle and Lerner (1955) found 0.006 percent Sc in a limestone residue and in a carbonate residue, and Goldschmidt and Peters (1931b) reported 3 ppm Sc in *Globigerina* ooze.

See also tables 1 and 19.

Selenium

The Se content of carbonate rocks from the western United States appears to vary with the amount of organic matter present although not all carbonaceous rocks are Se-rich. It also seems to be independent of clay and phosphate content (Beath et al., 1937; Knight and Beath, 1937; Beath et al., 1939). Lighter colored phosphate rock contains less Se than the darker, confirming the importance of organic matter. Se concentrations are observed in limonite concretions from the Niobrara Formation (table 13), but those from the Steele and other formations are not particularly Se-rich (see Goldschmidt, 1937, on the concentration of Se in sedimentary iron ores). The Se in the limonite concretions must be a secondary accumulation, but it is possible that Se in organic matter was concentrated by plants analogous to those that concentrate Se today.

The Se contents of six high-carbonate samples from Bartlett Deep cores (Edgington and Byers, 1942) were all less than 0.08 ppm, and similar samples from North Atlantic cores typically contained 0.1 or 0.2 ppm Se.

Silver

Wagoner (quoted in Clarke, 1924) reported 0.2 ppm Ag in two marbles from California and Carrara, Italy. Higazy (1954) reported 1 and 4 ppm Ag in two limestones that he examined.

See also tables 22, 27, 28, and 30.

Strontium

Most of the Sr introduced into carbonate sediments is substituted for Ca in calcite and, more especially, aragonite. Smaller amounts precipitate as SrSO_4 in environments of evaporite deposition. H. C. W. Skinner (personal communication) reported that small percentages of celestite occur in the chemical precipitate of dolomite and magnesian calcite being formed today in certain shallow lakes of South Australia. Odum (1950, 1951a) confirmed by X-ray diffraction the presence of celestite reported, on the basis of optical and chemical tests, in the skeletons of some Acantharian radiolaria (see literature review by Vinogradov, 1953, for example). As Odum pointed out, however, the skeletons are quantitatively insignificant as sources of Sr. Not only pure celestite, but also solid solutions of SrSO_4 with BaSO_4 occur in sedimentary rocks (Grahmann, 1920; Dragunov and Katchenkov, 1953).

The distribution of most of the celestite found in carbonate rocks, like that of barite, suggests secondary redistribution. It occurs as nodular masses, coatings on cavern walls, in geodes, and as replacing bodies containing masses of unaltered or slightly altered limestone (Phalen, 1914; Evans, 1946a). Less clear is the distribution in rocks like the members of the Peacock Formation of late Permian age in Nolan County, Texas (Evans, 1946a), that contain considerable celestite disseminated as individual grains in the carbonate rock as well as roughly alternating bands of celestite and dolomite in some places.

As much as 0.1 percent celestite is found in the Röt near Jena, in the lowest gypsum and in the Rhizocorallum Dolomite, occurring as 0.1 to 0.5 mm grains in the rock and as crystals on the walls of cavities from which fossils have been dissolved out (Kalkowsky, 1921). At a number of localities in New York, Ohio, and Michigan, disseminated crystals and small circular spots of celestite occur in typical fine-grained Bass Island Dolomite of Silurian age that is devoid of fossils and

is part of an evaporite sequence containing salt and anhydrite beds (Kraus, 1904, 1905; Kraus and Hunt, 1906). Cavities with smooth faces are left when the celestite crystals are removed. The crystals are not vug fillings, but are believed to have formed when the rest of the rock had not yet solidified. One such compact dolomite contains 14.3 percent celestite (analysis 86, Part IV). At Maybee, Michigan, and Put-in-Bay, Ohio, much of the celestite has been dissolved away, leaving characteristic casts. It apparently was redeposited, together with gypsum and native sulfur, in its present position, partially filling open spaces in lower lying cavernous beds (see also Morrison, 1935).

Vinogradov and Borovik-Romanova (1945), on the basis of analyses of a dolomite-anhydrite sequence from Kazan, suggested that Sr is concentrated toward the top of a carbonate layer and in anhydrite. Sr increases to an average of 2.57 percent in 29 samples of the dolomites and anhydrites of the celestite-containing Lower Kungur beds of early Permian age from the Buguruslan region (Katchenkov, 1952), compared with averages ranging from 0.003 to 0.65 percent in adjoining beds.

The occurrence of redistributed celestite is not limited to dolomites. Celestite has been observed as a coarsely granular replacement of a pelletal calcite mudstone of the Calciferos Sandstone Series of Carboniferous age, North Berwick, East Lothian, Scotland (Geol. Survey Great Britain, 1956). The rock contains as much as 25 percent of material insoluble in cold dilute HCl, practically all of it celestite. Knopf (1918) described a recrystallized Miocene age limestone from near Barstow, California, containing some strontianite and a minor amount of celestite as a microscopic constituent. The specimen, which analyzed 39.5 percent CaO and 12.9 percent SrO, is apparently not typical, for the marls and algal limestones that occur in similar lacustrine evaporite series in California do not carry obvious amounts of Sr minerals, even though there may be actual strontianite or celestite beds a short stratigraphic distance away (Durrell, 1953).

Crandallite, a hydrated Ca-Al phosphate of the alunite structural type that is formed in the soil profile and elsewhere during weathering by the interaction of phosphatic solutions with argillaceous limestones, acts as a scavenger for the concentration of Sr (Fron del, 1958).

The Sr content of 49 clams of Recent age examined ranged from 660 to 5000 ppm, average 1570 ppm, and that of 47 Recent age snails from 860 to 2700 ppm, average 1390 ppm (Turekian and Armstrong, in press). For these mollusks, Turekian and Armstrong concluded that the particular genus is more important in defining Sr content than is the calcite/aragonite ratio.

Thompson and Chow (1955) determined by flame photometry the Sr/Ca ratio for cleaned, air-dried skeletons of some 250 modern carbonate-secreting marine organisms. The results, summarized in table 14, are thus for varied mixtures of organic material and carbonate skeleton. The Sr/Ca atom ratios vary from 1.0 to 11×10^{-3} and are less than Thompson and Chow's value for sea water, 8.9×10^{-3} (Odum, 1951a, gives 9.23×10^{-3}), except for the *Nudibranchia* and *Madreporaria*. Variations in the ratio are according to phylogenetic classification, with the qualification that aragonitic material generally has a higher ratio than calcite (table 15). Salinity of sea water did not affect the ratio; Chow and Thompson (1955a, 1955b) showed that various sea waters have a constant ratio between Sr and chlorinity, and Ca and chlorinity, so that the Sr/Ca ratio of the water should be constant regardless of salinity. They found no evidence of seasonal fluctuation or variation with the age of the organism (see also Kulp, Turekian, and Boyd, 1952). Data on similar modern faunas from arctic and equatorial marine waters show that the temperature of the sea water changes the ratio only insofar as it may lead to a change

in the CaCO_3 polymorph secreted by the organism (see also Kulp, Turekian, and Boyd, 1952; Odum, 1957; Lowenstam, 1954a). Lowenstam (1954a) showed that the percentage of SrCO_3 in the skeletal carbonate of the Serpulidae is directly proportional to the percentage of aragonite in these materials.

Odum's experiments (1950, 1951a) in which snails (*Physa*) were grown in environments of varying Sr and Ca concentrations showed that the Sr/Ca ratio in the shells of these mollusks, made up of a mixture of aragonite and strontianite crystals rather than a solid solution, is proportional to the Sr/Ca ratio in the environmental water over a range of 10,000 units of Sr/Ca. A plot of the Sr/Ca ratios of aragonitic mollusks against the Sr/Ca of natural waters also yields a straight line (Odum, 1950). This proportionality is the self-regulating mechanism (Odum, 1951b) that has acted to stabilize the Sr geochemical cycle and maintain the Sr/Ca ratio of the ocean at about the same order of magnitude since at least early Paleozoic time, as indicated by similar Sr/Ca ratios in fossils and their modern taxonomic counterparts. Analyses by Odum of six modern *Venus* clams from the same mudflat showed 35 percent variance in the Sr/Ca ratio, so significant variation in comparing Sr/Ca values of fossils with those of modern counterparts must be at least outside the range 65 to 135 percent. Of some 26 Sr/Ca values for fossils sealed in shale or asphalt, only two fell outside the range, and these, 55 and 62 percent, were just below it. Aragonitic nautiloids from an asphalt deposit of Pennsylvanian age in Oklahoma had Sr/Ca values that were 92 percent of those of comparable modern forms; brachiopods of Ordovician and Devonian age had values of 80 to 105 percent.

Odum (1957) showed that organisms with rapid circulatory and efficiently functioning excretory systems, and little or no tissue separating the calcification surface from the sea, have the lowest steady state Sr/Ca concentrations in the media around the calcification site and consequently the lowest Sr/Ca ratios.

Organisms of today deposit a higher proportion of aragonite relative to calcite than those of Paleozoic time, which should lead to an enhanced Sr/Ca content in marine sediments, other things being equal. Murray (1954) showed that Sr was one of several elements that enhanced the formation of aragonite from solution relative to that of calcite. Turekian and Kulp (1956) emphasized the suggestion of Trueman (1942) that the abundance of Sr in an environment might determine whether calcite or aragonite would be the preferred form. Such is certainly not always the case, as Odum (1950) pointed out, for freshwater mollusk shells with low Sr/Ca ratios are aragonitic.

There is little or no overlap in the ranges of Sr/Ca values found for marine versus freshwater aragonitic pelecypods, gastropods, calcitic algae, and decapods (Odum, 1957). Therefore, Sr/Ca ratios of diagenetically unaltered fossil skeletal material can be used to determine whether the organisms grew in marine (or saline lake) waters or in fresh water. The Sr/Ca ratio would be expected to rise with continued inflow into basins having high evaporation to outflow ratios, and, indeed, high Sr/Ca ratios are noted by Odum for skeletal material from such lakes (table 17). Diagenesis decreases the Sr/Ca ratio of fossil carbonate, and the difference between the ratios for matrix and for skeleton in a given rock should be a measure of the amount of alteration.

Kulp, Turekian, and Boyd (1952) analyzed 153 carbonate rocks spectrographically and obtained an over-all average of $\text{Sr/Ca} = 0.71 \times 10^{-3}$ (table 18). The Sr content of fossils was found to vary greatly, but they generally contained twice as much Sr as the surrounding carbonate matrix, a result attributed both to the probable presence of some inorganic, low-Sr carbonate in the matrix and to more rapid Sr

loss from the finer grained matrix because of more rapid aragonite-to-calcite transformation of fossil fragments. Goldberg (1957) stated that CaCO_3 inorganically precipitated from sea water is aragonite with a Sr/Ca ratio greater than that of sea water. According to Goldberg, recrystallization of fossils, the great majority of which originally have a Sr/Ca ratio less than that of sea water, should lead to lowered Sr/Ca values only if it takes place in nonmarine waters of reduced Sr/Ca ratios.

The progressively lower Sr contents of calcites from the basin, forereef, and backreef areas of the Steinplatte reef complex of Austria, 380 to 1570, 150 to 420, and 60 to 150 ppm Sr, respectively, were attributed by Sternberg et al. (1959) to more thorough recrystallization away from the basin.

Kulp, Turekian, and Boyd (1952) detected no trend of Sr/Ca values with geologic age in analyses of 63 North American carbonate rocks ranging in age from Precambrian to Tertiary, because variable amounts of recrystallization apparently had taken place in rocks of the same age. However, the analyses of carbonate rocks from the Russian Platform (Vinogradov et al., 1952) (fig. 2) showed a definite decrease in Ca/Sr ratios from the Permian to the Tertiary, which would suggest that Sr lost from fossils during recrystallization is in general not retained locally as celestite, and that the number of samples taken (some 3600) was sufficient for obtaining a statistically valid increase in the amount of recrystallization with geologic time. Examination of the plots of the percentage of CaSO_4 and that of Sr (fig. 3) show that the high post-Permian values are unrelated to chemically precipitated celestite associated with anhydrite (and evaporite dolomite), as appears to be the

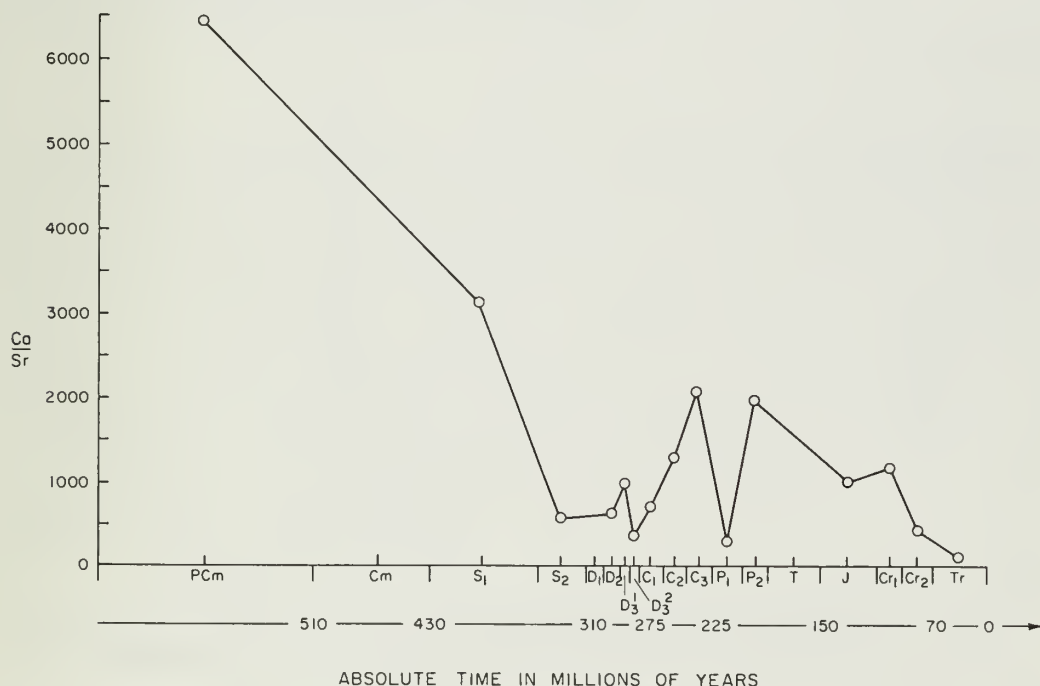


Fig. 2 - Variation with time of the Ca:Sr ratio in carbonate rocks of the Russian Platform (Vinogradov et al., 1952), based on 94 composite analyses of 3563 samples.

case with the early Permian and some of the Devonian Sr maxima. The latter maxima coincide with several of the pre-Mesozoic points for samples in figure 2 that fall below the apparent general trend line and illustrate the inability of a simple Ca/Sr ratio to depict a situation in which Sr is being contributed in two different forms, one quite independent of the carbonate crystal structure, and in which Ca is present both as calcite and anhydrite. The additional criticism may be made that the value of Ca should be increased by an amount corresponding in mol percent to the Mg present in dolomite. For both evaporite dolomite and replacive dolomite the important quantity to be measured is the amount of carbonate mineral formed concurrently with the original Sr deposition. The use of a (Ca + Mg)/Sr ratio would have improved the quality of the fit of the points in figure 2 to a straight line.

Dolomites apparently may contain either less or more Sr than limestones, depending upon whether celestite is present. Stout's analyses of Ohio dolomites (1941) showed a bimodal Sr distribution in which the low-Sr dolomites have no celestite and the high-Sr ones do (Odum, 1950). Scotch dolomites contain markedly less Sr than Scotch limestones (table 19). Kulp, Turekian, and Boyd (1952), on the other hand, found a fair positive correlation between the percentage of Sr and that of Mg in Indiana limestones.

The abundance of Sr^{87} is increasing with geologic time because of the decay of Rb^{87} (see Tilton and Davis, 1959). Wickman (1948) proposed that the Sr^{87} content of marine carbonates and shells, which quite effectively reject Rb and take Sr

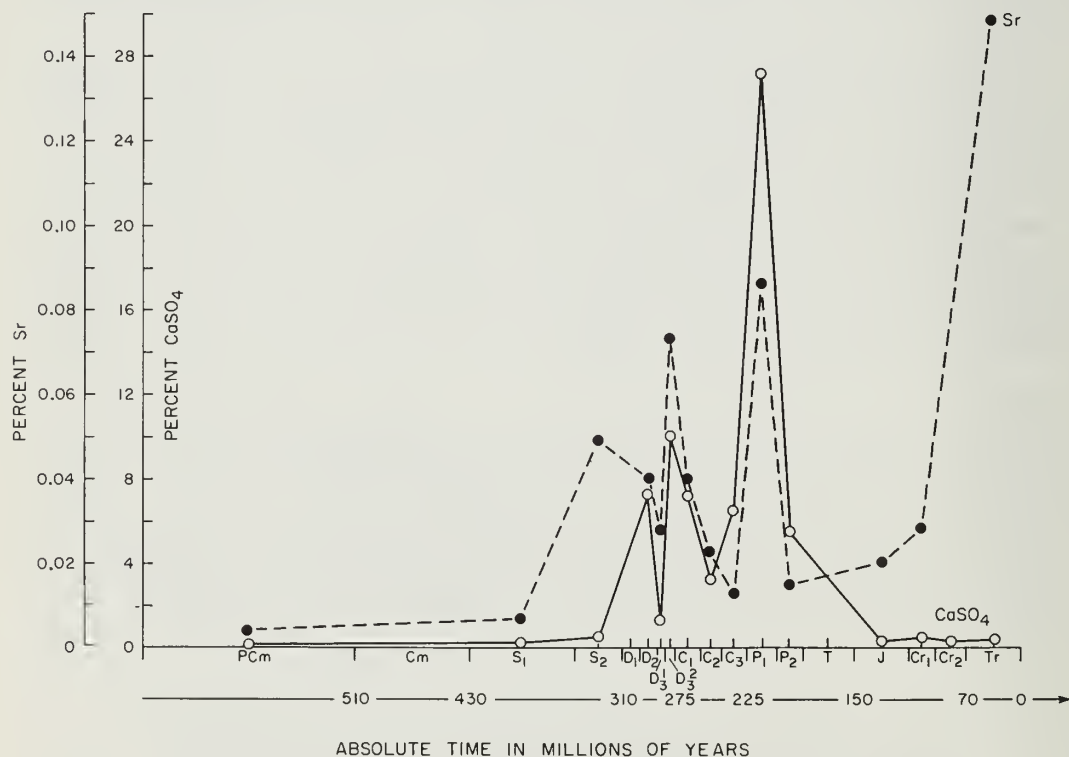


Fig. 3 - Variation with time of the CaCO_3 and Sr contents of carbonate rocks of the Russian Platform (Vinogradov et al., 1952), based on 97 composite analyses of 3659 samples.

into solid solution, be used to measure their geologic age. Gast (1955) gave probable $\text{Sr}^{86}/\text{Sr}^{88}$ values ranging from 0.1206 to 0.1213 for four limestones, but did not cite his absolute values for $\text{Sr}^{87}/\text{Sr}^{88}$ and $\text{Sr}^{87}/\text{Sr}^{86}$. Ewald et al. (1956) reported $\text{Sr}^{86}/\text{Sr}^{88}$ values of 0.1195 and 0.1196 for limestones of Cambrian and Devonian age; the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios given were 4.86 ± 0.90 and 3.00 ± 1.10 , respectively. Interpretation of these results is complicated by isotopic fractionation during the mass spectrometric analysis. Gast concluded that the Sr^{87} increase with time was too slight to permit accurate measurement. Ewald et al. found that the ages obtained were always greater than the geologic ages of the samples.

See tables 1, 16, 19, 23, 26, 27, 28, 30, and 31.

Thallium

A limestone and a dolomite examined spectrochemically by Shaw (1952) contained less than 0.05 ppm Tl. A sample of *Globigerina* ooze from $02^\circ 44' \text{ S}$, $92^\circ 45' \text{ W}$ showed 0.16 ppm.

Tin

A limestone from Mansjo, Sweden, examined by Higazy (1954), contained 10 ppm Sn. Wedepohl (1955) found 3 to 5 ppm Sn in composites of 93 German limestones, 0.8 ppm in a specimen of *Arca* from the beach at Gaybu-Pernambuco, 2.6 ppm in a sea-urchin test from the beach at Bahia, 0.7 ppm in calcareous algal material from the beach at San Carlos, Fernando Po.

See also tables 19, 22, 28, 29, and 30.

Titanium

The average Ti content, on a carbonate-free basis, for *Meteor* samples containing 50 to 60 percent CaCO_3 is 0.74 percent (estimated from graph in Correns, 1941). Samples with 60 to 70 percent CaCO_3 contained 0.87 percent Ti, those with 70 to 80 percent CaCO_3 showed 0.59 percent, and those having more than 80 percent CaCO_3 had 0.61 percent Ti, indicating that the Ti percentage is independent of CaCO_3 content. The over-all average for 178 *Meteor* samples, on a carbonate-free basis, is 0.70 percent. Titanium is concentrated mostly in the coarser fractions, and is capable of migration, as is shown by the formation of authigenic anatase. Even when the organic silica diluent as well as the carbonate content is calculated out, the percentage of Ti fluctuates markedly both laterally and vertically in these samples, which suggested to Correns differences in vulcanism or in climate and consequently in weathering processes during glacial time.

The Ti content of Pacific pelagic sediments decreases away from the Hawaiian Islands basaltic pyroclastic source (Goldberg and Arrhenius, 1958). Ti occurs in these sediments principally in augite.

An aragonite-magnesite assemblage from Lake Bonneville sediments, Utah (Graf et al., 1959; unpublished data), contained 360 ppm Ti, and three samples of dolomite sediment contained 370, 450, and 330 ppm. The average Ti content of 22 limestones from the northern Tuscan Apennines was 264 ppm (Pieruccini, 1951).

Marine siderite ores examined by Landergren (1948) contained 2000 ppm Ti. Noddack and Noddack found only 1 to 8 mg Ti per ton in sea animals.

See also tables 1, 22, 25, 26, 28, 29, 30, and 35.

Tungsten

Jeffery (1959) found 0.2, 0.6, 0.4, and 0.7 ppm W in four sedimentary limestones from Uganda, 0.5 ppm in a calcite derived secondarily from a carbonate.

Vanadium

Fragmentary information is available about certain mechanisms involved in the sedimentary geochemical cycle of V, but it has not yet been possible to evaluate their quantitative importance in the total cycle. V is concentrated in the blood of some ascidians and holothurians, and is carried in petroleum as a porphyrin complex. Evidence for a positive correlation between V and organic matter in carbonate rocks is conflicting. LeRiche (1959) found such a correlation for shale and argillaceous limestones of the Lower Lias of southern England, but demonstrated by detailed study of one of the samples that the V was associated with clay minerals. He suggested that V might have been transferred to the clay from organic matter.

Hillebrand (1900) found 0.004 percent V_2O_5 in a composite of 498 carbonate building stones. Two dolomites from Broken Hill, Rhodesia, had 3 and 5 ppm V (Taylor, 1954), and Higazy (1954) found 6 and 10 ppm V in limestones from Uganda and Sweden, respectively. An aragonite-magnesite assemblage from Lake Bonneville sediments, Utah (Graf et al., 1959; unpublished data), contained 13 ppm V, and three samples of dolomite sediment had 12, 15, and 10 ppm. Anosov and Chukrov (1948) reported an average of 0.0034 percent V_2O_5 in the "carbonate rocks" associated with ore deposits in central Kazakhstan. Katchenkov and Flegontova (1955) detected 0.014, 0.001, and 0.0001 percent V in three of six Devonian argillaceous limestones from the Volga-Ural area they examined. Jost (1932) used a potentiometric titration method and reported <0.001 percent V in 29 of the 30 limestones he examined. A marl from the Hauptbleiglanzbank of the Gipskeuper at Eutendorf had 0.0036 percent V. Fersmann (1929) reported 0.0022 percent V_2O_5 in a limestone from Tyuya-Muyun, Turkestan, containing 0.28 percent insoluble residue, 0.0011 percent V_2O_5 in calcite from the same place, 0.0039 percent V_2O_5 in bituminous calcite from the same place, and 0.0101 percent V_2O_5 in a bituminous limestone from Aravan. All of the V_2O_5 in Fersmann's first sample remained in the acid-insoluble fraction, and is presumed to have been in clay minerals.

An enhanced V content in bituminous carbonate rocks is also shown by Jost's analyses of thin, dark, very argillaceous limestones that occur interlayered in the Lias near Reutlingen. Five samples contained 0.0048, 0.0025, 0.0026, 0.0016, and 0.0012 percent V. There is a fair correlation for these samples between the percent of V and weight loss on heating, but not between the percentage of V and the percentage of ignited HCl-insoluble residue, which suggests that the V is associated with organic matter rather than with clay minerals. Bituminous limestones and dolomites from the Urals and the near-Volga area examined by Romm (1946) contained from 18 to 119 ppm V, whereas nonbituminous carbonate rocks had, at most, only a trace of V.

Seven Paleogenic limestones from North Ferghana contained from <1 to 5350 ppm V (Proshliakov, 1958). Stylolitic fillings and hard bitumens in the rocks showed from 40 to 27,300 ppm V, and in only one case was the V in the rock as a whole more concentrated than that in the filling. Small, black, acicular, V-containing crystals are reported to occur in the bitumen. There is no apparent relation between the amounts of V and of insoluble residue, but fairly positive correlations are shown between V and sulfide sulfur and between V and total organic matter. The residue

obtained on evaporation of ground water from oxidized, bitumen-free rocks in this area contains thousandths to hundredths of a percent V; almost no V (<0.001 percent) is observed in the residue from waters traversing unoxidized gray rocks.

The sedimentary siderite ores described by Landergren (1948) contained an average of 70 ppm V.

The V content of Pacific pelagic sediments decreases away from the Hawaiian Islands basaltic pyroclastic source (Goldberg and Arrhenius, 1958). V occurs in these sediments in magnetite, ilmenite, and ferromagnesian minerals.

See also tables 19, 22, 23, 24, 25, 28, 30, 34, 36, and 37.

Zinc

Wedepohl computed an average Zn value of 0.0024 percent from values obtained for limestones of the Muschelkalk in the vicinity of Göttingen (Wedepohl, 1953) and Jena (Heide and Singer, 1950). The only skeletal material of those listed in table 20 to have a striking Zn content is the sample of *Globigerina* tests.

Enrichment of Zn by plants is striking; coal ashes may contain 1 to 2 percent Zn and ashes of various recent plants may have 0.5 to 1.0 percent Zn. Clay minerals, in which the Zn is readily accommodated in interlayer positions, and plant residues are likely hosts for Zn in impure limestones.

See also tables 1, 22, 26, 28, 29, 30, 32, 33, and 34.

Zirconium and Hafnium

The Zr content of eight limestones and dolomites analyzed by Adams and Weaver (1958) ranged from 20 to 340 ppm (average 145 ppm). The insoluble residue ranged from 0.7 to 54 percent (average 11.9 percent) and there was a positive correlation between the percentage of Zr and the percentage of insoluble residue. However, if a similar plot is made for the much larger number of sedimentary and metamorphic carbonate rock analyses given by the Geological Survey of Great Britain (1956), there is a very wide scatter of points. Only the region of high Zr content and low insoluble residue percentage is essentially free of points, for example, Zr contents greater than 25 ppm at 0 percent HCl-insoluble, greater than 85 ppm at 10 percent, and greater than 150 ppm at 20 percent.

Degenhardt (1957) determined Zr colorimetrically with Alizarin-S and computed 19 ppm as the average Zr content of limestones, 17 ppm for dolomites. The entire Zr content of carbonate rocks generally is found in the insoluble residue in the clay minerals, as zircon relicts, and in Zr-bearing rutile, sphene, apatite, magnetite, ilmenite, and amphiboles and pyroxenes. However, the oolitic limestone from Auschnippetal and the Korallenoolith from Freden (table 21), which contain 1 ppm and 0.5 ppm, respectively, of Zr soluble in 0.2 N HCl, also contain appreciable amounts of iron oxide with which the Zr is believed to have been adsorptively bound. The amount of Zr in marine organisms is related by Degenhardt to the amount of Fe they contain. The Zr content of the two *Globigerina* oozes varies directly with the amount of acid-insoluble residue.

The Hf contents of these materials is very slight and within the limits of errors of determination.

See also tables 19 and 23.

THE ABUNDANCE OF MINOR ELEMENTS

Rankama and Sahama (1950) and Krauskopf (1955) made estimates of the average abundance of minor elements in carbonate rocks. Their values together with a set based upon the information contained in this circular are presented in table 38. These estimates are, of course, highly subjective, because for only a few elements such as Sr, Th, and U is sufficient information available to allow even the most rudimentary statistical analysis. Evaluation of the various analysts and analytical techniques also is very difficult. Some of the emission spectrographic results for V may be high because of the vanadium-calcium line coincidence recently discussed by Shaw (1958) and by Scott and Swaine (1959). The concentrations of most of the elements vary with the purity of carbonate rock concerned, and no good estimate of the relative abundances of various impure carbonate rock types is available to permit the weighting of an average abundance properly.

In spite of these difficulties, there are a number of encouraging agreements between workers studying the distribution of the same element in sample suites from different local areas. Willett (1950), the Geological Survey of Great Britain (1956), and Ronov (1956) examined carbonate rocks from New Zealand, Scotland, and the Russian Platform, respectively, and found the same average Co concentration, 4.3 ppm. The Scottish rocks contain an average of 420 ppm Sr, the Russian ones 480 ppm, those from eastern Kansas (Runnels and Schleicher, 1956) 490 ppm, and a suite of limestones from the Pennsylvanian of Illinois (Ostrom, 1957) 490 ppm. Degenhardt (1957) found for German samples an average value of 19 ppm Zr in limestones and 17 ppm in dolomites, and the Geological Survey of Great Britain found the Scotch rocks contained an average of 16 ± 3 ppm Zr. The agreement between the values for U and Th in carbonate rocks from the Russian Platform and the United States (tables 9 and 10) is excellent, especially as the somewhat greater Th content of the Russian rocks correlates with a higher insoluble residue content. The average values for Ni of the sample sets from Scotland, the Russian Platform, eastern Kansas, and the Pennsylvanian of Illinois (11 ± 1 , 7.5, 9.0, and 17 ± 0.9 ppm) lead to an over-all estimate of 12 ± 5 ppm.

Shaw's (1957) estimated average of 4 ppm Ga in carbonate rocks is supported by the average value of 2.2 ± 1.2 ppm found for the Scottish rocks. The rocks from the Russian Platform contain an average of 440 ppm Cl, compared with a figure of about 480 ppm obtained by averaging the various Cl values given in table 6. The 320 ppm F found in the Scottish rocks is in excellent agreement with a value of about 315 ppm found by averaging the assorted F values given in table 6. Wedepohl's (1953) average of 24 ppm Zn in German carbonate rocks is supported by averages of 19 and 24 ppm for sample sets from Romania (Savul and Ababi, 1956; Savul and Movileanu, 1956), by a value of 28 ppm in unmineralized Lockport dolomite (Cannon, 1955) from New York state, and by an average of 34 ± 2 ppm for a group of dolomites of Ordovician age from Missouri (Keller et al., 1950). Ostrom's high average Zn value may result from an unusual abundance of organic matter in the limestones of Pennsylvanian age that he examined. The average of 9 ppm Pb in German carbonate rocks (Wedepohl, 1956) is in good agreement with an average of 7.2 ± 4.2 ppm for the Scottish rocks, 8.0 ± 0.5 for those from eastern Kansas, and 13 and 14 ppm for the Romanian sample sets.

Examination of average values given by the various workers for other elements in carbonate rocks reveals discrepancies of as much as an order of magnitude. No explanation of this lack of agreement is at present possible.

APPENDIX

TABLES

Table 1. - Enrichment of Specific Elements in Mineralized Lockport Dolomite
Drill Hole 10, Orleans County, New York
(After Cannon, 1955. Semiquantitative spectrographic analyses
in ppm by A. T. Meyers and P. J. Duncan)

Element	Unmineralized Lockport Dolomite ppm	Mineralized Lockport Dolomite ppm
Fe	5,000	15,000
K	3,000	3,000-8,500
Ti	50-500	1,500
Sr	50-85	50-5,000
Zn	28*	580*
Pb	8*	120*
B	20	25-65
Ba	2-15	15-50
Cr	2-9	25-45
Cu	2-9	15-50
Ni	2-9	15-85
Y	0	5-15

* Averages of chemical analyses by H. Bloom. At another place, Cannon quotes weighted averages of Bloom's determinations for drill hole 10 as 0.688% (688 ppm) Zn, 0.0022% (22 ppm) Pb.

Table 2. - Authigenic Compounds Found in the Green River Formation
(After Milton, 1957; Milton and Eugster, 1959;
Milton and Fahey, 1960)

The capitalized entries are unique to the Green River Formation; those in italics are known elsewhere only in igneous or metamorphic rocks. Bassanite and anhydrite may have formed in wet drill cuttings during storage.

<i>Acmite</i> $\text{NaFe}^{+++}\text{Si}_2\text{O}_6$	LOUGHLINITE $(\text{Na}_2,\text{Mg})_2\text{Si}_3\text{O}_6(\text{OH})_4$
Albertite Hydrocarbon	Magnesite MgCO_3
Albite $\text{NaAlSi}_3\text{O}_8$	Marcasite FeS_2
Alstonite $\text{CaBa}(\text{CO}_3)_2$	Nahcolite NaHCO_3
Analcite $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	Natron $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Anhydrite CaSO_4	NORSETHITE $\text{BaMg}(\text{CO}_3)_2$
Barite BaSO_4	Northupite $\text{Na}_3\text{MgCl}(\text{CO}_3)_2$
Bassanite $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$	Ozokerite Hydrocarbon
Barytocalcite $\text{CaBa}(\text{CO}_3)_2$	Pirssonite $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$
BRADLEYITE $\text{Na}_3\text{Mg}(\text{PO}_4)(\text{CO}_3)$	Pyrite FeS_2
Burbankite $\text{Na}_2(\text{Ca},\text{Ba},\text{Sr},\text{La},\text{Ce})_4(\text{CO}_3)_5$	Pyrrhotite $\text{Fe}_{(1-x)}\text{S}$
Calcite CaCO_3 , often magnesian	Quartz SiO_2
Collophane (fossils). Variable, approximates $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3) \cdot \text{H}_2\text{O}$	REEDMERGNERITE NaBSi_3O_8
<i>Cryolite</i> Na_3AlF_6	<i>Riebeckite-magnesianriebeckite</i> $\text{Na}_2(\text{Mg},\text{Fe}^{++})_3(\text{Fe}^{++},\text{Al})_2\text{Si}_8\text{O}_{22}(\text{OH})_2$
Dawsonite $\text{NaAl}(\text{CO}_3)(\text{OH})_2$	Searlesite $\text{NaBSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$
Dolomite $\text{CaMg}(\text{CO}_3)_2$	Sepiolite $\text{Mg}_2\text{Si}_3\text{O}_6(\text{OH})_4$
Eitelite $\text{Na}_2\text{Mg}(\text{CO}_3)_2$	SHORTITE $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$
<i>Elpidite</i> $\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$	Siderite FeCO_3
Fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3) \cdot \text{H}_2\text{O}$	Tabbyite Hydrocarbon
GARRELSITE $(\text{Ba},\text{Ca},\text{Mg})\text{B}_3\text{SiO}_6(\text{OH})_3$	Thermonatrite $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
Gaylussite $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$	Trona $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$
Gilsonite Hydrocarbon	Uintahite Hydrocarbon
Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Utahite Hydrocarbon
Ingramite Hydrocarbon	UNNAMED NaMg fluoride
<i>Labuntsovite</i> $(\text{K},\text{Ba},\text{Na},\text{Ca},\text{Mn})(\text{Ti},\text{Nb})$ $(\text{Si},\text{Al})_2(\text{O},\text{OH})_7 \cdot \text{H}_2\text{O}$	UNNAMED $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$
<i>Leucosphenite</i> $\text{CaBaNa}_3\text{BTi}_3\text{Si}_9\text{O}_{29}$	Witherite BaCO_3
	Wurzite ZnS

Table 3. - Range and Average Content of Ni, Cu, and Co in Some Carbonate Sediments Determined by Radioactivation Analyses (Smales et al., 1957) unless otherwise noted

	Four limy Black Sea silt (Mal- yuga, 1949)*	Globi- gerina oozes†	Short core (B. Kullenberg)‡	Long core 1° 10' N., 19° 50' W. (B. Kullenberg)§	Red clay	Average igneous rock**	Average meteorite**
Ppm Ni (range, av.)	23-54 (35.8)		15 samples 9.1-68 (34)	9 samples 11.6-55 (28)			
Ppm Cu (range, av.)	45-110 (65)		10 samples 25-79 (48.5)	6 samples 20-98 (48)			
Ppm Co (range, av.)	6.6-16.5 (13.3)		15 samples 3.2-15.3 (8.1)	9 samples 2.3-33 (10.5)			
Ni/Co (range, av.)	2.1-3.6 (2.8)	34 samples 1.0-7.0 (4.0)			13 samples 1.4-7.1 (3.4)	3.5	13.1
Ni/Cu (range, av.)	0.45-0.78 (0.59)	24 samples 0.4-1.6 (0.8)			13 samples 0.4-1.4 (0.8)	1.1	92
Cu/Co (range, av.)	2.7-7.5 (5.2)	24 samples 2.0-10.9 (5.4)			1.3-7.3 (4.4)	3.0	0.14

* Fourteen samples of limy silt contained from 50.37 to 72.47% CaCO_3 (av. 58.7%) (Strakhov, 1947).

† Sample set includes three with less than 50% CaCO_3 , seven with percentage CaCO_3 not specified.

‡ CO_2 content corrected for sea salt ranges from 31.74 to 39.56%.

Not including samples with CaCO_3 content unknown or less than 50%.

** From Rankama and Sahama (1950).

Table 4. - Barium in Calcareous Sediments, Rocks, and Shells
(von Engelhardt, 1936, except as noted)

Material analyzed	Barium (ppm)
Composite of 32 Devonian age limestones, Germany	110
Composite of 45 Jurassic age limestones, Germany	83
Composite of 16 Cretaceous age limestones, Germany	190
Highly pure <i>Mucronata</i> limestone, Kvarnby near Malmö, Sweden	3-10
Flint from <i>Mucronata</i> limestone, Malmö, Sweden	50
Fetid limestone, Upper Zechstein, Wartberg near Kassel	30-100
Plattendolomit, Upper Zechstein, Wichtelstein near Witzhausen	1-3
Three Limestone layers in the <i>Ceratites</i> beds (Triassic age), near Kassel	10-30
Clayey interlayer in the <i>Ceratites</i> limestone (Triassic age), near Kassel	300-1000
Fossil-rich <i>Trochites</i> limestone (Triassic age), near Kassel	10-30
Clayey, fossiliferous, somewhat bituminous middle Muschelkalk (Triassic age), near Kassel	30-100
Average of 90 composite analyses of 3530 original samples of carbonate rocks from the Russian Platform (Vinogradov et al., 1952)	50
Average of 5 Cambro-Ordovician age dolomites, Missouri (Winslow and Robertson, 1894)	24
Average of 9 limestones of Mississippian age, Missouri (Winslow and Robertson, 1894)	27
Limestones, Germany (Prashnowsky, 1957)	52, 90, 260, 60, 40
Range and average for 49 clams of Recent age (Turekian and Armstrong, in press)	4-41 (12)
Range and average for 45 snails of Recent age (Turekian and Armstrong, in press)	4-15 (7)
Range and average for 11 corals of Recent age (dry weight) (Bowen, 1956)	8-85 (27)
Range and average for 14 Mollusk shells of Recent age (dry weight) (Bowen, 1956)	<1-48 (9±2.5)*
Range and average for 29 fossil corals (Bowen, 1956)	<5-251 (28±4)*

* Variation in average results from uncertainty in real values for samples having quantities below the limit of detection.

Table 5. - Content of B, Ga, and Rb in Insoluble Residue of Limestone from the Allegheny Series of Pennsylvanian Age (Compiled from Degens et al., 1958)

	B (ppm)		Ga (ppm)		Rb (ppm)	
	Range	Av.	Range	Av.	Range	Av.
Marine, fossiliferous Vanport and Putnam Hill Limestones						
(a). Insoluble residue (6 values)	4-80	42	<2-7	2.5 ± 0.7*		
(b). < 2 μ fractions of insoluble residue (10 values)	133-1200	360	7-40	20	100-1100	480
Nodular fresh water Freeport and Upper Kittanning Limestones; in clay below coal seams; contain small coiled gastropods, spores, and fresh water ostracodes						
(a). Insoluble residue (6 values)	20-70	48	8-70	19		
(b). <2 μ fraction of insoluble residue (8 values)	30-90	67	25-120	73	80-650	360

* The range given measures only the uncertainty resulting from possible assumed averages for the quantities below the limit of detection.

Table 6. - Halogen Content of Carbonate Organisms, Sediments and Rocks
(in parts per million)

Material analyzed	Fluorine*	Iodine	Chlorine†		Bromine†		P ₂ O ₅	Remarks
			Total	Water-leachable	Total	Water-leachable		
Wellenkalk, Dransfeld	220						360	
Recent calcareous tufa, Lenglern, near Göttingen	100		20		10.2	5.5	150	Sufficient P ₂ O ₅ to account for all F (Correns, 1956)
Chalk, Rügen	280		2000		3.9		880	
Cenomanian pläner, Kaierde, Hils, Lower Saxony	20		120		2.3		1140	Sufficient P ₂ O ₅ to account for all F (Correns, 1956)
Oolitic limestone, Weissjura, Fréden a. d. Leine, Lower Saxony	60		180		6		760	Sufficient P ₂ O ₅ to account for all F (Correns, 1956)
Laminated marl, Diemarden near Göttingen	1780		210		5.5	1.7	1370	
Ceratites limestone, mo ₂ , Upper Muschelkalk, Diemarden near Göttingen	510		240		4.9	1.6	1260	About 1.5% illite (Füchtbauer 1950); estimate remaining 370 ppm F in CaF ₂
Oolitic zone, mu, Lower Muschelkalk, near Göttingen	190		50		6.8		350	
Floury natural solution residue of mica and dolomite from inside shells, Lower Muschelkalk, Göttingen	800		500		8.3		860	360 ppm Cl goes into solution by dissolving dolomite in warm 2N nitric or acetic acid; leaves 300 ppm in mica
Zechstein dolomite, Scharzfeld, Harz	110		610		7.5	2.8	70	
Zechstein reef dolomite, Römerstein b. Bad Sachsa, Harz (fluorite-bearing)	250		880		15	3.4	300	Less than 2% insoluble; all Cl into solution in acid; CaF ₂ may have migrated
Crinoidal limestone, Reckershausen near Göttingen (Correns, 1956)	20						380	Data indicate no F incorporated into crinoid stem columnals that make up the rock (Correns, 1956)

<i>Globigerina</i> ooze, Meteor Sta. 240, depth 2271 m, 64.3% CaCO ₃ (Correns, 1937)	550	780	Est. 100 ppm F in mica, 70 in apatite, rest in CaF ₂
<i>Carnegie</i> collection of <i>Globigerina</i> oozes, range and average for 8 samples (Shepherd, 1940)	100-530 (330)		
Composite of 16 German Cretaceous age limestones (von Engelhardt, 1936)	270	2360	
Composite of 45 German Jurassic age limestones (von Engelhardt, 1936)	550	1970	
Composite of 32 German Devonian age limestones (von Engelhardt, 1936)	210	450	
Solenhofen Limestone, Upper Jurassic age	120	200	
Windsor Group limestones of Cape Breton, N. S. (Seraphim, 1951)	1500		Maximum F value, found in sandy fluorite-bearing layers of the Ribben limestone
Jurassic age limestone (Eberius and Kowalski, 1952)	700		Magnesian limestone, southwest Mabou
Devonian age limestone (Eberius and Kowalski, 1952)	90		Average for six other samples
Range and average for 30 lime- stones from northeastern U. S. (Jeffries, 1951)	530		
Argillaceous limestone (Shepherd, 1940)	320		
Two fossiliferous limestones from Maryland (Shepherd, 1940)	Trace-1030 (350)	3100-24900 [†] (11,100)	
	370		
	210		
	230		

Table 6. - Continued

Material analyzed	Fluorine	Iodine	Chlorine		Bromine		P ₂ O ₅	Remarks
			Total	Water-leachable	Total	Water-leachable		
Norwegian Ordovician age limestone (Barth and Bruun, 1945)	200							
30 Japanese limestones, range 0-200 and av. (Kokubu, 1956)	300							
Calcareous sand, <i>Meteor</i> Sta. 219, 220 m. depth (Correns, 1937)	190							
29 Limestones and Dolomites from Illinois (Lamar and Shrode, 1953), range and av.** Limestones								
							30-300 (120)	
							230-1000 (450)	
Dolomites								
Russian limestones and dolomites (Danilova, 1949)	239							
Dolomite, Carey, Ohio (Graf, 1952)							300	
Dolomite composite, Silurian age (Niagara), Kankakee, Illinois (Graf, 1952)							550	
Dolomite, Silurian age (Niagara), Manteno, Illinois (Graf, 1952)							310	
Devonian carbonate rocks (Gulyaeva, 1951b)							970	
<i>Lithothamnium</i>								170,1800
Smooth coral								200

	1400	1200
Branched coral	310	
Calcareous algae [*]		5.9
Limestones, mean values for Vereisk horizon, Saratov-Near Volga region (Itkina, 1956)	4.0	
Various Swiss limestones (von Fellenberg, 1924)	.25-.75	
Triassic age Rötti dolomite (von Fellenberg, 1924)	1	
Maltis limestone of the Kinzigpasshöhe, Malm (Late Jurassic age) (von Fellenberg, 1924)	1.76	
Effingerschichten, Malm (Late Jurassic age) (von Fellenberg, 1924)	5.4	
Malm (Late Jurassic age) of Württemberg (Wilke-Dörffurt, 1927; quoted by Correns, 1956)	up to 6.6	
Range and average for 4 Devonian age limestones (Gulyaeva, 1951a)	2.9-5.6 (3.9)	
* Koritnig, 1951, unless otherwise noted.		
† Behne, 1953, unless otherwise noted.		
‡ P ₂ O ₅ given for only eight samples.		
** Leachable sulfate, limestones, 10-1840 ppm, average 380 ppm; dolomites, 60-770 ppm, average 280 ppm.		

Table 7. - Cobalt in Calcareous Rocks

Material analyzed	Cobalt (ppm)	
	Range	Average
14 limestones, Southland, N. Z.*	2.4-6.6	4.0
5 samples of limestone from Otago, N. Z.*	0.2-0.4	0.3
6 limestones, Southland, N. Z.†	3-5	3.3
Limestones from Nelson, N. Z.†	0.2-4.2	1.3
Limestones from Canterbury, N. Z.†	1.0-12.5	2.5
Limestone from Westland, N. Z.†	0.6	
Average for 3 limestones from Otago, N. Z.†		0.6
Kaka Limestone, Nelson, N. Z. ^α	not detectable	
°Mid-Tertiary age limestones, N. Z. ^α	0.98-12.4	4.35
Average values for vertical series of limestone samples through lime quarries, N. Z. ^α	3.37, 2.7, 4.39, 3.12, 2.87, 2.09, 3.25, 0.98	
Average value for determination in Willett's and Stanton's studies ^α		4.26
Pleistocene age limestone, North Island, N.Z.**	1.0	
Average for Oligocene age limestones, north Island, N.Z.**		1.3
Average for Pliocene age limestones, North Island, N.Z.**		2.1
Average for Eocene age limestones, North Island, N.Z.**		4.9
Six Ordovician limestones, Unmetamorphosed or slightly metamorphosed, Sweden‡	<1-7	1.9 ± 0.2
Same, but omitting sample with 7 ppm Co, which has local enrichments in Fe and is believed to have undergone ancient surface weathering	<1-2	1.0 ± 0.2
U. S. Bureau of Standards dolomite, no. 88 ^{αα}	0.37	
U. S. Bureau of Standards argillaceous limestone, no. 1a ^{αα}	0.61	
U. S. Bureau of Standards limestone, no. 4976 ^{αα}	0.8	
Marine siderite ores ^{°°}	300	

* Dixon and Kidson (1940).

† Stanton (1944).

α Willett (1950).

° Average composition, 86.1% CaCO₃, 3.42% Al₂O₃ and Fe oxides, 0.93% MgO, 6.79% SiO₂, 0.14% P₂O₅.

** Maunsell (1945).

‡ Lundegårdh (1949).

αα Carr and Turekian (1959).

°° Landergren (1948).

Table 8. - Lead in Calcareous Organisms, Sediments, and Rocks*

Material analyzed	Pb (ppm)
32 German Devonian age limestones	9
45 German Jurassic age limestones	10
16 German Cretaceous age limestones	7
HCl-insoluble residues of above entries	30
Wellenkalk near Göttingen	15
Dolomite, Permian age (Zechstein), Scharzfeld, Harz	5
9 Muschelkalk limestones near Jena ^α	7.5
4 Oberen Röt limestones near Jena ^α	11
4 Limestones from Indonesia [°]	9
6 Cambrian and Ordovician age limestones, Missouri** (range, trace to 0.00156%)	9.9 ± 0.3†
7 Lower Carboniferous age limestones, Missouri** (range, trace to 0.00346%)	12.5 ± 0.5†
9 Silurian and Ordovician age carbonate rocks, 8 highly dolomitic; insoluble residue 1.55 to 11.63% (av., 4.91%) Dubuque County, Iowa‡ (range, 0.00060 to 0.00587%)	33
Mississippian age Leadville Limestone, Colorado, 50 samples near ore, 75 from unaltered limestone ^{αα}	3
Average for samples from eupelagic Atlantic core Al80-76 containing 78 percent CaCO ₃ ^{°°}	4
<i>Arca</i> , Gaybu-Pernambuco beach	1.4
<i>Spirula</i> , Praia Granda, Saint Vincent	1
Sea urchin test, Bahia beach	2.7
<i>Lithothamnium</i> , beach at San Carlos, Fernando Po	0.8
<i>Globiğerina</i> , Meteor Station 240a	360
<i>Globiğerina</i> , Albatross Station 360	6
<i>Globiğerina</i> , Albatross Station 355	29
<i>Globiğerina</i> ooze, Meteor Station 261	170
<i>Globiğerina</i> ooze, Meteor Station 288b	250

* Wedepohl, 1956, except as noted.

† Range results from uncertainty of real values for samples having quantities below the limit of detection.

^α Heide and Lerz (1955).[°] Van Tongeren (1938).

** Winslow and Robertson (1894).

‡ Calvin and Bain (1900).

^{αα} Engel and Engel (1956).^{°°} Turekian and Feely (1956).

Table 9. - Uranium and Thorium in Carbonate Rocks of the Russian Platform
(Baranov, et al., 1956)

Composites	Number of samples in composites	Percent insoluble residue	Thorium		Uranium		Th/U
			(ppm)	(ppm)	(ppm)	(ppm)	
Silurian	10			4.6	2.3	2.3	2.0
Devonian	53			2.8	1.6	1.6	1.7
Carboniferous	43			1.2	2.7	2.7	0.4
Permian	13			1.3	3.3	3.3	0.4
Jurassic	2			4.7	2.3	2.3	2.0
Cretaceous	4			2.2	1.9	1.9	1.3
Tertiary	3			7.1	3.6	3.6	2.0
Over-all mean values*				2.4	2.1	2.1	1.1
Over-all median values*				2.7	2.3	2.3	1.6

* Computed by Adams and Weaver (1958)

Table 10. - Uranium and Thorium in North American Carbonate Rocks
(Adams and Weaver, 1958, except as noted)

	Insoluble residue			Uranium (ppm)			Thorium (ppm)			Thorium/Uranium		
	wt %			Mean			Mean			Range		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
54 individual samples (Precambrian through Cretaceous)			0.1-6.6*	2.2	1.4	0.04-6.5	1.7	1.1	0.05-60	1.2		0.9
25 aggregates (516 samples, Precambrian through Tertiary)	8.5	6.1		2.2	1.5		1.1	1.1		0.7		0.5
11 individual samples (Precambrian through Pleistocene) (Bell, 1956)			0.7-38	1.9								

* Plus one exceptional Atlantic Coast marine limestone of Triassic age with 18 ppm Uranium.

Table 11. - Uranium and Thorium in Miscellaneous CaCO_3 -rich Samples
(After Sackett, 1958)

Material analyzed	Uranium (ppm)	$A_{\text{U}238}$ A ²³⁸ onium	Th ²³² (calc.)
Aragonitic oolites	3.2		
<i>Lithophyllum craspedium</i> , Bikini (calcitic)	0.37 \pm 0.04	<0.01	
<i>Tridacna</i> , collected alive (aragonite)	0.1 \pm 0.02	<0.1	
<i>Porites australiensis</i> Vaughan, collected alive (probably aragonitic)	2.5 \pm 0.2	<0.01	
Aragonitic coral, <i>Favia</i>	1.83		
Hydrocoralline deposit (<i>Millepora</i>) on above coral	0.42		
Modern gastropod, Cook Inlet, Alaska	0.32 \pm 0.03	<0.01	
Two mollusks	0.28, 0.38		
Eniwetok beach rock, C ¹⁴ date, 2700 \pm 250 years	1.35 \pm 0.07		
Shell fragments, Bootlegger Cove, Alaska, estimated age 40,000 to 60,000 years	0.26 \pm 0.03		
Marine shells, estimated ages 4,000 to 9,000 years	0.11 \pm 0.01 0.14 \pm 0.01 0.24 \pm 0.02 0.044		
Marine shells, C ¹⁴ ages of six samples are between 4,000 and 12,000 years; one sample 35,000 years old	Range: 0.12-1.36 Av., 0.51		
Sample 389A, mainly CaCO_3 , from atop North Atlantic seamount, estimated age 8,500 years	0.41 \pm 0.03		
Sample 303, land snail shells, Folsom culture	1.4 \pm 0.1		
Pennsylvanian age limestone	0.8 \pm 0.1		
Mississippian age limestone	1.02 \pm 0.05		0.14 \pm 0.01*
Snail shells from Lahontan and Bonne- ville Lake basins	0.23		0.08
Calcareous tufa from Lahontan and Bonneville Lake basins	18.3, 1.03, 2.84, 1.09 0.86, 1.04 1.05		6.7, 0.2, 0.8, 0.3, 0.3, 0.08, 0.7

* By activation.

Table 12. - Thorium and Uranium Content of Carbonate Rocks, Sediments, and Invertebrate Skeletal Materials

Material analyzed	Thorium (ppm)	Uranium (ppm)
<i>Globigerina</i> ooze*	0.11-0.15	
Dolomite, Serpiano†		4.7, 4.6
Dolomite, Verrucano†		3.5
Freshwater Paleozoic age limestone†		15
Posidonien Schiefer, Liassic age†		2, 10, 10, 12
Fossiliferous zone in dolomite, Serpiano†		8
CaCO ₃ precipitated from sea water in the laboratory‡		2.6, 3.2, 3.2, 4.6
Marine calcareous invertebrate hard parts†		
Three calcitic forms		0.17, 0.18, 0.041
Six aragonitic forms		0.009, 0.21, 0.012, 0.067, 0.022, 0.028
Seven forms containing both calcite and aragonite		0.046, 0.021, 0.013 0.014, 0.004, 0.032 0.044
Two aragonitic forms now partly altered to calcite		2.5, 3.2

* Koczy (1950). † Erlenmeyer et al. (1950). ‡ Tatsumoto and Goldberg (1959).

Table 13. - Selenium Content of Some Carbonate Rocks Mostly from the Western United States

Material analyzed	Selenium (ppm)	
	Range	Average
Eight limestones interbedded with shale, Provo Canyon, Utah*	0.4-2.6	1.0
"Oil Shale," Green River Formation†	0.32	
Limnolite concretions, Niobrara Formation ^a	23-548	
Limestone, Phosphoria Formation, Rocky Point, near Cokeville, Wyo.; contains 4.90% P ₂ O ₅ ^o	14.3	
Limestone, Upper Frontier Formation, Teton County, Wyo. ^a	6.68	
Limestone, Thaynes Formation, western Wyo. ^a	1.54	
Fossiliferous, argillaceous limestone, Graneros Formation, late Cretaceous age, Shannon County, S. D.**	0.7, 1.5	
Five samples of limestone, Fort Hayes Member, Niobrara Formation, S. D.‡	0.0-3.0	0.97
Three samples, Fort Hays Member, Niobrara Formation, Trego County, Kan.**	0.3-6.0	2.3
Three samples, Mobridge Chalk of the Pierre Formation, S. D. ^{aa}	6.4, 15.0, 0.86	
Chalky marl of the upper part of the Niobrara Formation, S. D. ^{aa}	0.31	
Calp Limestone, Ireland ^{oo}	0.97	

* Beath et al. (1939). ^o Beath et al. (1937) ^{aa} Searight and Moxon (1945).

† Beath et al. (1935). ** Byers (1936). ^{oo} Walsh and Fleming (1953).

^a Knight and Beath (1937). ‡ Moxon et al. (1938)

Table 14. - Strontium Content (in Percent) of Carbonate-Secreting Marine Organisms
(After Thompson and Chow, 1955)

Classification	No. of samples	Calcium		Strontium		CO ₂		Organic matter		Sr/Ca x 1000	
		Range	Av.	Range	Av.	Range	Av.	Range	Av.	Range	Av.
Marine Algae, Corallinaceae	9	23.6-29.2	27.4	0.151-0.219	0.193	30.8-36.5	34.2	14.0-29.8	18.5	2.93-3.45	3.20
Protozoa, Foraminifera	3	31.4-33.3	32.1	0.193-0.239	0.216	40.1-40.8	40.6	5.19-9.40	7.10	2.78-3.28	3.07
Porifera, Calcareae	3	13.5-29.6	18.9	0.098-0.149	0.115	23.3-35.8	31.2	12.7-25.0	20.2	2.30-3.34	2.99
Demispongiae	5	0.05-0.08	0.06	trace		1.97-12.6	5.91	38.2-85.0	49.7		
Coelenterata, Hydrozoa	10	35.7-38.8	37.4	0.224-0.930	0.711	38.5-43.1	41.0	2.50-8.46	4.16	2.73-11.2	8.69
Anthozoa											
Alcyonaria	5	4.72-37.3	23.2	0.039-0.618	0.229	12.4-41.8	30.5	2.38-37.5	22.0	2.64-7.57	4.04
Zoantharia	7	32.3-37.9	36.5	0.666-0.868	0.789	37.5-41.5	41.0	2.90-8.84	4.40	8.85-10.7	9.86
Annelida, Polychaeta	6	29.2-35.4	32.5	0.247-0.596	0.421	34.2-42.5	39.1	5.20-15.0	6.84	3.86-8.24	5.87
Arthropoda, Cirripedia	17	32.4-39.1	36.3	0.282-0.428	0.354	36.7-41.8	40.8	1.80-12.3	4.65	3.77-5.28	4.45
Decapoda	7	21.2-28.0	24.6	0.278-0.371	0.328	25.7-32.5	29.3	20.0-33.3	27.8	6.00-6.69	6.17
Mollusca, Amphineura	15	37.0-38.8	38.0	0.606-0.751	0.669	39.6-42.2	41.2	3.06-6.10	4.30	7.32-9.25	8.06
Pelecypoda	64	33.7-39.4	37.9	0.085-0.248	0.154	37.6-43.1	41.8	1.54-13.3	3.18	1.01-2.98	1.85
Gastropoda											
Prosobranchia	53	35.5-39.9	37.8	0.104-0.204	0.139	39.4-42.8	41.8	1.13-7.10	3.14	1.25-2.48	1.68
Opisthobranchia	2	2.60-3.16	2.88	0.062-0.063	0.062	3.25-4.68	3.97	67.2-78.0	72.6	9-11	10
Scaphopoda	1	38.2		0.196		42.3		1.81		2.35	
Cephalopoda	1	35.8		0.293		40.1		7.35		3.74	
Bryozoa, Ectoprocta	8	18.2-35.7	30.4	0.124-0.307	0.228	23.7-40.2	35.4	6.28-36.0	14.7	3.00-3.94	3.41
Brachiopoda, Articulata	5	37.7-38.9	38.4	0.102-0.130	0.113	41.3-42.8	42.3	1.79-3.02	2.12	1.20-1.57	1.36
Echinodermata, Crinoidea	1	25.8		0.145		38.2		13.3		2.56	
Asteroidea	18	17.2-27.3	22.4	0.101-0.162	0.134	24.9-37.7	31.8	19.0-39.4	29.3	2.60-2.89	2.73
Ophiuroidea	8	20.4-31.2	26.3	0.118-0.185	0.153	28.9-39.2	34.6	11.0-33.4	20.5	2.63-2.79	2.69
Echinoidea	12	30.5-36.4	33.6	0.178-0.218	0.199	39.6-43.9	41.8	1.20-9.28	5.00	2.46-2.89	2.70
Holothuroidea	3	25.2-29.1	27.8	0.153-0.170	0.166	32.1-38.3	35.0	12.2-25.8	18.3	2.72-2.78	2.74
Chordata, Ascidiacea	2	0.30-0.38	0.34	trace		13.5-13.8	13.7	69.1-70.0	69.6		

Table 15. - Average Sr/Ca Atom Ratios, Times 1000, Contrasted for Calcitic and Aragonitic Skeletal Materials
(After Thompson and Chow, 1955)

Calcite (excluding aragonitic species)		Calcite-aragonite mixtures (excluding completely calcitic species)		Aragonite (excluding calcitic species)	
Algae, Corallinaceae	3.20	Mollusca		Coelenterata	
Protozoa, Foraminifera	3.07	Pelecypoda	1.94	Hydrozoa	9.49
Porifera, Calcarea	2.99	Gastropoda		Zoantharia	9.86
Coelenterata, Alcyonaria	3.16	Prosobranchia	1.68	Mollusca	
Arthropoda, Cirripeda	4.45			Amphineura	8.06
Mollusca				Gastropoda	
Pelecypoda				Nudibranchia	10
Anomiidae	1.22			Scaphopoda	2.35
Ostreidae	1.22			Cephalopoda	3.74
Pectinidae	1.31				
Bryozoa, Ectoprocta	3.41				
Brachiopoda, Articulata	1.36				
Echinodermata	2.71				

Table 16. - Strontium Content of Modern and Fossil Invertebrate Skeletal Material
(After Bowen, 1956)

Material analyzed	Strontium (ppm)	
	Range	Av.
15 Corals of Recent age	5590-13,400	9270
47 Fossil corals, Silurian to Tertiary in age*	154-8300	1210
14 Mollusk shells of Recent age		
2 amphineura	3950, 5600	
5 gastropods	1420-2340	1860
1 scaphopod	3550	
5 lamellibranchs	1810-3260	2160
1 cephalopod	2910	

* Four values greater than 4,000 ppm are all from Cretaceous or younger specimens; one of the Silurian corals contains 1780 ppm Sr.

Table 17. - The Sr/Ca Ratios of Selected Calcareous Organisms, Sediments, and Rocks
(Compiled from Odum, 1950, 1957, unless otherwise noted)

Identifications of calcite and aragonite in the invertebrate skeletal materials are in some cases based upon X-ray diffraction, and in others inferred from published mineralogical descriptions assumed to hold constant within taxonomic subdivisions, independent of environmental effects. Sea water has 9.23 atoms Sr/1000 atoms Ca (Odum, 1951a).

Description	Number of samples	Atoms Sr/1000 atoms Ca Range or average
Littoral calcareous sands	11	0.57-13.00 (Av. 5.59)
Pteropod ooze (32.7% Ca)	1	2.38
Foraminiferal ooze		
Surface to 1000 m (av. % Ca, 22.6)	4	2.61
1000 m to 4000 m (av. % Ca, 30.3)	8	1.49
Sediment (33.44% Ca) from humid lake	1	0.6
Marine chalks	3	1.49
Precambrian age limestones with highest Sr/Ca values	2	1.92
Other Precambrian age limestones	6	0.1-0.7
Fossiliferous limestones, Silurian to Pennsylvanian in age	8	0.92
Cambrian age limestones	8	0.3-1.2
Silurian age limestones	8	0.5-1.2
Miocene fossiliferous marl	1	2.78
Averages of skeletal components of limestones	5	4.64
Average for terrestrial limestones		2.68
Estimated value for diagenetically altered limestones		1.21
Cambrian and Ordovician age dolomites	13	0.40
Dolomites from Funafuti	5	0.82
Celestite-bearing dolomites of Ohio*	20	29.15
Celestite-free dolomites of Ohio*	176	<0.20
Limestones from evaporite deposit of Carboniferous age†	13	1.96
Dolomites from above evaporite series	36	11.44
Conemaugh freshwater limestone, Pennsylvanian age, Maryland		0.64
Solenhofen Limestone		0.46
		Noll, 1934; 0.50
Kootenai Formation, Cretaceous age, Elliston, Montana (contains freshwater snails)		0.51
Lebanon Limestone, Cretaceous age, containing freshwater arachnids		1.20
Freshwater limestone containing arachnids, Coconino County, Arizona		0.20
Miocene age lacustrine limestone, Florissant, Teller County, Colorado, containing insects		10.60
Skeletal materials formed in lakes with high evaporation/outflow rate or complete closure		
Calcareous algae, Lake Winnemucca, Nevada		3.53
Snail, Inya Lake, Burma		1.94

Table 17. - Continued

Description	Number of samples	Atoms Sr/1000 atoms Ca Range or Average
<i>Balimulus alternatus</i> , LaSal Vieja, Texas, chlorinity 16,710 ppm		2.31
<i>Succinea avara</i> , Gray Tom Lake, Texas		1.17
<i>Myxas ampula</i> , Pyramid Valley swamp, N. Z.		2.57
<i>Isodora acconori</i> , Pyramid Valley swamp, N. Z.		1.47
Organically formed amorphous CaCO ₃ from	1	(foot) 6.22
<i>Archidorus britannica</i> (verified by X-ray diffraction)		(mantle) 7.27
Organically formed calcite. Average for 18 groups of organisms		3.63
Organically formed aragonite. Average for 16 groups of organisms		6.09
Inorganic marine calcite precipitates	17	1.29
Inorganic marine aragonite precipitates	10	5.90
Rapid direct CaCO ₃ precipitate from sea water	5	11.30
Marine calcitic algae	9	3.96
Aragonitic marine algae (<i>Halimeda</i>)	1	10.80
Calcitic freshwater algae	3	0.52
Littoral foraminifera	5	2.07
Calcitic marine sponges	3	3.82
Aragonitic marine coelenterates		
Hydrozoa--Millepora	1	11.02
Anthozoa--Hexacoralla	16	10.80
Anthozoa--Octocoralla-- <i>Heliopora</i>	1	8.06
Calcitic marine Octocoralla	3	4.10
Aragonitic marine serpulid	1	3.10
Calcitic marine bryozoa	4	3.96
Calcitic marine brachiopods (Telotrema)	2	1.81
Mollusks		
Aragonitic marine amphineura	2	9.01
Aragonitic marine pelecypods	6	2.63
Calcitic marine pelecypods	6	1.65
Aragonitic freshwater pelecypods	23	0.87
Aragonitic freshwater gastropods	21	0.75
Aragonitic marine gastropods	8	2.31
Aragonitic marine scaphopods	2	2.35
Aragonitic marine cephalopods	3	4.86
Calcitic marine cephalopods	1	4.60
Marine decapods (calcite and amorphous CaCO ₃)	8	6.03
Freshwater calcitic decapods	1	0.62
Calcitic marine echinoderms		
Asteroidea	2	3.71
Echinoidea	3	3.06
Ophiuroidea	2	3.47
Crinoidea	1	3.38
Holothuroidea	1	2.60
Iron carbonate nodules, Middle Lias, England†		4.4
Aragonitic otoliths of marine teleosts	8	3.08
Calcitic eggshell, chicken	1	0.32
Calcitic eggshell, fish-eating bird	3	0.57
Calcitic eggshell, invertebrate-eating bird	2	2.40

* Stout (1941).

† Vinogradov and Borovik-Romanova (1945).

‡ Taylor (1950).

Table 18. - Strontium: Calcium Ratios of Some Calcareous Organisms,
Sediments, and Rocks
(Compiled from Kulp et al., 1952, unless otherwise noted)

Description	Number of samples	Atoms Sr/1000 Ca Range	Ca Av.
Average for 155 limestones		0.71	
Limestones*		0.63	
Brachiopods and carbonate matrices (Ordovician-Permian in age)	15		
Matrices		0.16-1.49	0.51
Brachiopods		0.41-1.83	1.03
Average for samples from eupelagic Atlantic core A180-76; 31.3% Ca, 1600 ppm Sr†		2.34	
Average for 10 samples from Atlantic deep- sea core A180-74; 28.2-39.6% Ca (av. 35.0%), 1550 to 2560 ppm Sr (av. 2075 ppm)‡		2.71	
<i>Globigerina</i> ooze, Pacific Ocean (37.5% Ca, 0.122% Sr, 41.8% CO ₂ , 1.46% organic matter)*		1.49	
Deep-sea sediments, Indian Ocean (Swedish Deep Sea Exped., 1948-1949)(29.4% Ca, 0.125% Sr, 37.7% CO ₂ , 2.95% org. matter)*		1.94	
Fossils from the Calvert Formation, Miocene age, Plum Point, Maryland			
Average for 155 fossils examined		3.10	
12 gastropods		2.12-3.21	2.68
9 pelecypods		2.05-6.57	3.19
1 scaphopod		3.88	
1 annelid tube		12.0	
North American carbonate rocks			
Precambrian age	10	0.17-2.45	0.99
Cambrian age	1	0.25	
Ordovician age	10	0.33-1.33	0.71
Silurian age	1	1.19	
Devonian age	15	0.11-0.71	0.29
Mississippian age	7	0.12-1.73	0.49
Pennsylvanian age	4	0.40-1.30	0.84
Permian age	4	0.18-0.67	0.35
Triassic age	3	0.39-3.12	1.66
Jurassic age	1	0.45	
Cretaceous age	5	0.27-1.33	0.55
Tertiary age	2	1.09-1.50	1.30
Limestones from Indiana			
Pennsylvanian age, 2.63-6.44% MgCO ₃ , av. 4.54**	2	0.73-0.92	0.82
Mississippian age, 0.80-5.66% MgCO ₃ , av. 2.23**	9	0.29-0.65	0.46
Devonian age, 4.45-38.6% MgCO ₃ , av. 16.2**	5	1.03-3.90	2.50
Silurian age, 1.04-41.1% MgCO ₃ , av. 15.8**	9	0.82-2.66	1.55
Ordovician age, 2.82-12.2% MgCO ₃ , av. 6.12**	3	0.61-1.69	1.04

* Thompson and Chow (1955).

† Turekian and Feely (1956).

‡ Turekian and Kulp (1956).

** Individual MgCO₃ values from Patton (1949).

Table 19. - Minor Element Composition of Scottish Sedimentary Carbonate Rocks
(Compiled from Geol. Survey of Great Britain, 1956)

Element	Sensitivity (ppm)	Total obser- vations*	Percentage of observations below sensi- tivity limit	Range (ppm)	Average (ppm)
B	1	29	31	<1-6000	320
Ba	5	183	8	<5-8000	220
Co	5	183	83	<5-35	4.3 ± 1.8†
Cr	2	183	12	<2-100	13
F	Not stated	6		200-700	320
Ga	3	183	80	<3-10	2.2 ± 1.2†
La	25	183	90	<25-50	14 ± 11†
Li	1	183	7	<1-1000	37
Ni	5	183	45	<5-60	11 ± 1†
Pb	10	183	84	<10-80	7.2 ± 4.2†
Rb	30	183	75	<30-800	60 ± 11†
Sn	10	Four samples show 10, 10, 20, and 20 ppm			
Sr	10	183	0.5	<10-6000	420
Sr (analyses with <10% MgO)		130	0.7	<10-6000	484
Sr (analyses with >10% MgO)		52‡	0	10-600	134
V	10	183	64	<10-150	12 ± 3†
Y	20	183	81	<20-80	13 ± 8†
Zr	10	183	61	<10-200	16 ± 3†

* Those samples are considered for which either a percent insoluble determination or values for CaO, MgO, and CO₂ are available to indicate that the material is a carbonate rock in the sense of this paper.

† The range specified measures only the uncertainty due to possible assumed averages for the quantities below the limit of detection.

‡ Omitting one value of 6000 ppm, which is 10 times the next larger value.

Table 20. - Zinc in Calcareous Organisms, Sediments, and Rocks
(Wedepohl, 1953, except as noted)

Material analyzed	Zinc (ppm)	
	Av.	Range
32 German Devonian age limestones*	33	
45 German Jurassic age limestones	22	
16 German Cretaceous age limestones	15	
6 Cambrian and Ordovician age dolomitic limestones, Missouri†	42.5	tr.-15.4
7 Lower Carboniferous age limestones, Missouri†	12±1 ^a	tr.-25.5
9 Silurian and Ordovician age carbonate rocks, including 8 highly dolomitic; insoluble residue 1.55-11.63% (av. 4.91%), Dubuque County, Iowa**	3.5±0.5 ^a	n.d. to 13.6
Cenomanian beds, Kaierde, Hils	7	
Korallenoolith, Delligsen, Hilsmulde	7	
Dolomite from Korallenoolith, Delligsen, Hilsmulde	4	
Zechstein Hauptdolomit, Scharzfeld, Harz	10	
Aragonite-magnesite assemblage, Lake Bonneville sediments‡	25	
3 dolomite samples, Lake Bonneville sediments‡	25, 31, 20	
Mississippian age Leadville Limestone, Colorado, 50 samples near ore, 75 from unaltered limestone***	10	
4 limestones of the unmetamorphosed Mississippian age Lake Valley Formation, Hanover District, N. M.††	35±6, 12±3, 22±6, 55±12	
Sedimentary siderite, Southern Sweden‡‡	40	
<i>Globigerina</i> -rich red clay, Albatross Station 359 (50% CaCO ₃)	58	
<i>Globigerina</i> , larger than 200 μ diameter, above sample	180	
<i>Globigerina</i> -rich clay, Meteor station 242 (48.3% CaCO ₃)	60	
Calcareous clay, Meteor station 242 (41% CaCO ₃)	23	
Sea urchin, Bahia	16	
Branching coral, St. Isabella, Fernando Po	13	
Serpulite, St. Vincent	12	
<i>Arca</i> , Gaybu-Pernambuco beach	1	
<i>Janthina</i> , Praia Granda, St. Vincent	≤3	
<i>Spirula</i> , Praia Granda, St. Vincent	≤2	
Calcareous algae, beach at San Carlos, Fernando Po	4	

* Wedepohl (1955).

† Winslow and Robertson (1894).

^a Range results from uncertainty of real values for samples having quantities below the limit of detection.

** Calvin and Bain (1900).

‡ Graf et al. (1959; unpublished data).

*** Engel and Engel (1956).

†† Barnes (1959).

‡‡ Palmqvist (1935).

Table 21. - Zirconium in Calcareous Organisms, Sediments, and Rocks
(Degenhardt, 1957, except as noted)

Material analyzed	Zirconium (ppm)
32 German Devonian age limestones	25
45 German Jurassic age limestones	12
16 German Cretaceous age limestones	18
Korallenoolith, Malm, Freden a.d. Leine	9
Solenhofen Plattenkalk, Malm, Solenhofen, Bavaria	18
Oolite zone from mu, Auschnippetal, Göttingen	20
Trochitenkalk, mo ₁ , Reckershausen, Göttingen	15
Ceratitenkalk, mo ₂ , Hainberg, Göttingen	30
Cenomanian beds, Kaierde, Hils	26
Quaternary age, calcareous tufa, Lenglern, Göttingen	23
8 North American limestones and dolomites*; Zr range 20-340 ppm; insoluble residue range 0.7-54%, av. 11.9%	145
Fluorite-bearing Zechstein Dolomite, Romerstein, Bad Sachsa, Harz	16
Zechstein dolomite, Scharzfeld, Harz	18
Arca, Gaybu-Pernambuco beach	< 2
Calcareous algae, beach at San Carlos, Fernando Po	8
<i>Globigerina</i> ooze, <i>Meteor</i> station 240a	10
<i>Globigerina</i> ooze, <i>Meteor</i> station 288b	30

* Adams and Weaver (1958).

Table 22. - Rare Elements in the Shell of Brissopsis lyrifera
(Noddack and Noddack, 1939)

Element	% dry wt.	Element	% dry wt.	Element	% dry wt.
Ti	0.00048	Zn	0.0065	Cr	2×10^{-6}
V	0.0005	Sn	0.00016	Mo	1×10^{-5}
Mn	0.053	Pb	0.0005	Au	7×10^{-7}
Fe	0.057	As	0.0008	Cd	3×10^{-6}
Co	0.0002			Th	1×10^{-7}
Ni	0.00021			Ge	7×10^{-5}
Cu	0.0018			Sb	1.8×10^{-5}
Ag	0.00015			Bi	3×10^{-6}

Table 23. - Minor Elements in Three Carbonate Rocks from Southern Finnish Lapland (Sahama, 1945)

Element	Limestone*	Dolomite*	Dolomite*
	412 (%)	438 (%)	470 (%)
MnO	0.003	0.05	0.05
BaO	0.07	0.03	0.01
SrO	0.1	0.1	0.1
B ₂ O ₃	0.003		0.003
Li ₂ O	0.0003		0.0003
Cr ₂ O ₃	0.0001	0.0003	0.01
V ₂ O ₅	0.0003		0.006
ZrO ₂			0.02

* It is not clear from the article whether these particular rocks are sedimentary.

Table 24, - Concentration of Some Minor Elements in Asphalts Compared with the Composition of the Carbonate Host Rocks (in ppm)
(Compiled from Erickson et al., 1954)

Material Analyzed	Uranium		Vanadium		Nickel		Copper	
	Asphalt	Rock	Asphalt	Rock	Asphalt	Rock	Asphalt	Rock
Petroliferous sandy limestone in Kaibab Limestone, Capitol Reef, Utah	3	3	15	15	15	15	7	2
Asphalt in vugs, Kaibab Limestone, Capitol Reef, Utah	0.5	3	120	0	120	tr.	1	tr.
Asphalt in vugs, Hermosa Formation, Gypsum Valley, Colo.	150	50	250	30	60	3	25	2

Table 25. - Minor Element Determinations for Some Swiss Carbonate Rocks
(in wt percent)
(Blumer and Erlenmeyer, 1950)

Material analyzed	SiO ₂	Fe	Ca	P	Ti	V	Mn	Ni	Mo	Loss on heating
Dalle nacrée, Montgremay	2.24	0.74	36.4	0.029	0.01	0.003	0.044	0.0002	*	*
Oolitic limestone, Wildegg	0.41	0.38	37.7	0.013	0.002	0.007	0.033	*	*	*
Oolitic limestone, Wildegg	0.27	1.31	37.8	0.018	0.006	0.005	0.039	0.001	*	*
Dolomite, Val Porina	0.078	0.23	21.6	0.007	0.003	0.002	0.011	0.0007	*	*
Dolomite, Serpiano	3.60	0.44	20.8	0.024	0.033	0.016	0.033	0.0073	0.0007	0.6
Spatiger Kalk, Schontal	3.75	1.29	36.0	0.25	0.043	0.012	0.10	0.0045	0.001	1.6
Encrinus, Liesbergmühle	26.2	0.39	26.8	0.035	0.003	0.010	0.004	0.0037	0.003	2.3
Bituminous dolomite, Serpiano	2.31	0.47	20.6	0.051	0.019	0.033	0.014	0.010	0.0007	2.5
Spatkalk, Bozen	7.37	2.8	28.8	0.12	0.063	0.024	0.094	0.0006	*	*
Spatkalk, Bozen	6.39	13.62	21.4	0.18	0.055	0.046	0.12	0.0001	*	*
Asphalkkalk, Val de Travers	0.04	0.18	36.1	0.013	0.011	0.006	0.006	0.0039	0.005	7.6
Bon Banc, Val de Travers	0.01	0.17	36.5	0.033	0.003	0.010	0.0095	0.010	0.0015	11.1
Marl, Wildegg	6.87	1.22	32.0	0.022	0.045	0.014	0.056	0.0002	*	*

* Determinations not carried out.

Table 26. - Minor Element Composition of 91 Samples of Pennsylvanian Limestones from Illinois
(Ostrom, 1957)

Element	Estimated accuracy*	Sensitivity (ppm)*	Percent of determinations below sensitivity limit	Range (ppm)	Average (ppm)
B	1/3X-3X		0	1-200	18
Ba	± 20%		0	10-10,000	260
Cr	± 15%		0	3-61	11
Cu	1/2X-2X		0	4-70	18
Mn			0	400-3700	1400
Mo	1/3X-3X	2	84	<2-20	1.8±1.0†
Ni	1/2X-2X	10	19	<10-70	17 ± 0.9†
Pb	1/2X-2X		0	6-100	26
Sr	20%		0	240-810	490
Ti		300	36	<300-2400	450 ± 50†
Zn	1/3X-3X	50	66	<50-700	63 ± 17†

* From Illinois State Geological Survey files.

† The range specified measures only the uncertainty due to possible assumed averages for the quantities below the limit of detection.

Table 27A. - Minor Elements in Dolomite Samples Containing Less Than 10 Percent Insoluble Residue, Believed to be Very Low in Calcite,
From One Illinois Quarry
(Lamar and Thompson, 1956)

Element	Number of analyses	Range (ppm)	Average (ppm)
B	14	6-16	10
Cu	14	0.5-4.6	2.0
Mn	14	330-4100	690
Pb	14	0.6-5.3	2.0

Table 27B. - Minor Elements in Limestone Samples Containing Less Than 10 Percent Insoluble Residue, From Two Illinois Quarries
(Lamar and Thompson, 1956)

Element	Number of analyses	Range (ppm)	Average (ppm)
Ag	47	0.31-3.9	1.2
B	40	1.9-11	4.6
Ba	47	5.8-270	15
Cu	47	1.2-17	6
Mn	47	37-3200	1000
Pb	46	1.0-5.1	2.5
Sr	47	110-630	220

Table 28. - Minor Element Composition of Ten Samples of Dolomite From The Jefferson City Formation of Ordovician Age, Marshfield, Missouri (Keller, et al., 1950)

Element	Range (ppm)	Average (ppm)
Ag	n.d.-0.5	0.31±0.01*
B	10-50	27
Ba	200-2000	620
Cr	50-2000	160
Cu	0.1-10	3.7
Pb	n.d.-3	1.1±0.3*
Mn	20-300	110
Mo	Two samples gave 20 and 30 ppm	
Ni	n.d.-5	2.7±0.2*
Sn	One sample gave 20 ppm	
Sr	200-3000	1270
Ti	1000-10,000	2700
V	n.d.-50	19±2*
Zn	n.d.-200	34±2*

* The range specified measures only the uncertainty due to possible assumed averages for quantities below the limit of detection. The authors estimate the determinations are accurate to ±50 percent of the amount present.

Table 29. - Minor Element Composition of Some *Globigerina* Oozes and *Globigerina* Samples from the Equatorial Atlantic (After Wedepohl, 1955)

	Mn	Cu	Zn	Sn	Pb	Ti	Ni	V
<i>Globigerina</i> ooze	2600	65	32	160	170	800	60	10
<i>Globigerina</i> ooze	880	94	6	70	250	1200	30	10
<i>Globigerina</i>	800	7.5	10	12	6	1500	10	
		7	180					
<i>Globigerina</i> , some sand	200	49	6	11	360	800	20	10
<i>Globigerina</i> , 10 percent sand	2000	20		1	29	1000		

Table 30. - Minor Element Composition of 277 Carbonate Rocks from Eastern Kansas for which the Sum ($\text{CaCO}_3 + \text{MgCO}_3$) \geq 50 Percent
(Compiled from Runnels and Schleicher, 1956)

Element	Range (ppm)	Percentage of observations below sensitivity limit	Average (ppm)
Ag	< 0.1-20	65	0.36±0.03*
B	< 0.5-300	68	4.5±0.2*
Ba	< 10-3000	83	82±4.2*
Cr	< 1-200	56	4.4±0.3*
Cu	0.13-500	0	5.6
Mn	20-6000	0	790
Mo	< 0.1-70	86	4.6±0.5*
Ni	< 0.5-100	13	9.0
Pb	< 1-200	49	8.0±0.5*
Sn	< 1-200	82	3.9±0.4*
Sr	14->2000	0†	490
Ti	< 10-6000	8	170 ± 0.3*
V	< 5-3000	9	55±0.2*
Zn	< 0.5-500	92	3±0.2*

* The range specified measures only the uncertainty due to possible assumed averages for the quantities below the limit of detection.

† Only 61 samples were analyzed for Sr, and all of these contained less than 10 percent MgO (see table 31 for comparison).

Table 31. - Minor Elements in Carbonate Rocks of the Russian Platform
(Compiled from Ronov, 1956)*

Element	Number of composites	Number of samples	Range of composite analyses (ppm)	Average of composite analyses (ppm)		Wt% Mg‡ composite analyses	
				Unweighted	Weighted†	Range	Average
Co	64	3067	0.9-1.5	4.5	4.3	0.5-12.6	Unweighted 5.8
Ni	64	3067	1.0-22	7.6	7.5		Weighted† 5.3
Cu	64	3067	8.2-87	23	23	Wt% insoluble residue: Range 0.70-41.84	
Cl	61	3015	280-800	430	440		
Sr	58	2927	20-2000	390	480		
Ba	59	2973	1-250	34.5	36	Unweighted av. 9.63	Weighted av.† 10.84

* The SO_3 percentages of a few composite analyses are high enough to indicate that some anhydrite (or gypsum) rocks are included in this compilation.

† The value for each composite analysis is counted in the average as many times as there are samples in that composite.

‡ Dolomite contains 13.2 wt percent Mg.

Table 32. - Minor Elements in Carbonate Rocks from the Eastern Carpathians, Roumania
(Compiled from Savul and Ababi, 1956; Savul and Movileanu, 1956)

Kind of Sample	Insoluble in HCl		Wt% dolomite calculated from chemical analysis		Elements*	Concentration (ppm)	
	Range	Av.	Range	Av.		Range	Av.
Triassic age dolomites	0.10-5.23	0.96	87.78-95.76	92.83	Zn (10)	6-45	24
					Pb (9)	3-41	14
					Cu (9)	0-33	6.9
	0.02-20.96	1.45	77.63-95.76	91.26	Mn (72)	0-626	146
Eocene age and Mesozoic age limestones	0.00-23.81	2.33	0.23-15.27	3.00	Zn (13)	4-52	19
					Pb (13)	0-31	13
					Cu (12)	0-30	13
	0.00-28.81	2.30	0.23-15.27	1.85	Mn (31)	9-422	93

* Number of samples in parentheses.

Table 33. - Ranges and Averages for Amounts of Minor Elements Extractable from
28 Agricultural Limestones of Western and Northwestern Germany
by Various Acid-Leaching Procedures*
(Schachtschabel and Schroeder, 1953)

Element	Range (ppm)	Average (ppm)
Mn	44-767	274
Zn	9-446	60.5
Cu	Trace-97	8.8
B	3-27	9.1
Co	0.2-12.5	4.0

* The limestones contained from 42.82 to 96.06% CaCO_3 , average, 84.54%, and 0.96 to 40.00% MgCO_3 , average 5.83%.

Table 34. - Ranges and Averages for Major and Minor Element Compositions of 60 Samples of Agricultural Limestone from the Atlantic Coast Region (Chichilo and Whittaker, 1958)

Chemical substance	Range (ppm)	Average (ppm)	Chemical substance	Range (%)	Average (%)
Mn	20-2320	240	CaCO ₃	48.80-98.07	76.29
F	< 5-1410	240	MgCO ₃	0.87-44.59	16.97
P	10-3600	213	Al	0.02-1.60	0.39
Zn	4-427	44	Fe	0.02-1.27	0.35
V	2-42	10	K	0.007-1.000	0.199
B	<1-18	3	S	< 0.01-0.38	0.10
Cu	< 0.3-5.2	1.1	Na	< 0.001-0.140	0.028
Mo	0.1-6.4	0.5			
Co	<1- 2	<1			

Table 35. - Amount of Minor Elements in 63 Samples Containing More than 20 Percent Ca* (Compiled from Landergren, 1955)

Element	Range (ppm)	Average (ppm)
Co	10-60	22
Cr	10-40	18
Fe	1.0-7.4†	2.1†
Mn	1000-6500	1810
Ni	20-130	58
Ti	600-2400	1520

* From a core taken at S 00° 07', W 18° 12'.

† In percent.

Table 36. - Distribution of Some Minor Elements in Eight Limestones from England and Scotland (Compiled from Hirst and Nicholls, 1958)

Element	Total amount		Percent of total amount insoluble in acetic acid*		Element in acid-insoluble fraction, as ppm of that fraction	
	Range (ppm)	Average (ppm)	Range (%)	Average (%)	Range (ppm)	Average (ppm)
Ni	4.3-83	27	5-86	55	7.9-190	89
Co	2.0-34	10	58-100	87	28-160	67
Cr	0.88-26	7.9	58-93	76	24-100	46
V	1.6-32	9.3	33-91	51	17-85	36

Ratios of values for individual elements

	Range	Average	Range	Average
Co/Ni	0.25-0.65	0.39	0.35-5.5	1.2
Cr/V	0.5-2.0	0.98	0.64-2.3	1.4

* Two samples contained 45 to 50% acid-insoluble material, one had about 15%, the others less than 6%.

Table 37. - Composition of Some Argillaceous Limestones in the Lower Lias of Southern England
(Compiled from Le Riche, 1959)

CaCO ₃ (%)	Mg* (%)	Mn* (%)	S* (%)	Oxidizable material as C* (%)	Mo* (ppm)	V* (ppm)	Cu* (ppm)	Ni* (ppm)	Co* (ppm)
48.0	4.17	0.16 (0.083)		2.25	15 (7.8)	230 (120)	25 (13)	87 (45)	29 (15)
53.7	1.66	0.20 (0.093)	3.33	2.01	<3 (<1.4)	220 (100)	15 (6.9)	75 (35)	17 (7.8)
55.9	1.69	0.07 (0.03)	2.92	10.2	7 (3)	200 (88)	53 (23)	100 (44)	31 (14)
57.1	5.00	<0.04 (<0.017)	2.49	2.26	<3 (<1.3)	280 (120)	27 (12)	91 (39)	22 (9.5)
71.6	6.03	0.17 (0.048)	2.57	5.95	22 (6.2)	220 (62)	44 (13)	78 (22)	12 (3.4)

* Calculated on a CaCO₃ - free basis. Values in parentheses are expressed in terms of the whole rock, including CaCO₃, for ease of comparison with other results similarly quoted.

Table 38. - Estimates of the Average Concentrations of Minor Elements in Carbonate Rocks

Element	Rankama and Sahama (1950) (ppm)	Krauskopf (1955) (ppm)	This paper (ppm)
Ag	0.2	0.2?	0.7 ± 0.4?
As			2.5 ± 1.0?
Au	0.005-0.009	0.005-0.009	0.005-0.009
B	3		12 ± 8?
Ba	120	20-200	150 ± 110
Be	0	<1	1
Br			7
Cd			0.1-0.2?
Cl	200		460
Co	0	0.2-2	4.3
Cr	2	5?	9 ± 4
Cs			4 ± 2
Cu	20.2	5-20	14 ± 9
F	250		320
Ga	3.7	3?	2.5 ± 1.5
Ge			0.09
Hg	0.03	0.03?	0.07
I			2.8
In		0.02?	
La			14 ± 11?
Li	26	2-20?	20 ± 17
Mn	385		500?
Mo		0.1-0.5?	1.1 ± 0.7?
Ni	0	3-10	12 ± 4
Pb	5-10	5-10	8 ± 4
Ra	0.42x10 ⁻⁶		
Rb	0	<100?	70 ± 40
Sb			0.2 ± 0.1?
Sc	0		0.3?
Se	<0.1	0.1-1?	0.1-1?
Sn			4?
Sr	425-765	400-800	475 ± 50
Th	1.1		1.9 ± 0.8
Ti			300 ± 150?
U	1.3		2.1 ± 0.2
V	<10	2-20?	15 ± 8?
W			0.5?
Y	0		13 ± 8?
Zn	≤ 50	4-20	26 ± 5
Zr			17 ± 4



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